# Handbook of Soil Acidity

edited by

Zdenko Rengel

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Preface

Soil acidity is one of the most prevalent problems in production of food and fiber because at least 40%, and by some estimates as much as 70%, of the world's arable land is affected. With increased pressure to produce more food for the expanding population of this planet and with urbanization claiming large chunks of arable land, agriculture is pushed more and more into marginal land plagued with edaphic and other stresses, including acidity.

Soils become acidic during geological evolution, especially in areas of high rainfall, because bases are relatively easy to leach from soils, leaving them acidic. In addition, soil acidification is frequently inevitable in agriculture that relies on either N_2 fixation or cheaper (ammonium-containing) N fertilizers and on export of organic material from paddocks, thus disturbing N and C cycles. In some parts of the world, acidification due to deposition of acidic rain is also important.

Although liming can effectively increase soil pH and thus ameliorate acidic soils, the large amounts required and the absence of lime pits positioned close to the paddocks where lime is needed make soil liming an expensive option in many situations. In addition, liming subsoil is technically difficult and may be economically unprofitable in many soils. Therefore, other management options need to be employed either in isolation or together with liming to allow continuity of food and fiber production on land with a high acidification potential.

There are four subject areas in this book: (1) soil acidification (global distribution of acidic and acidifying soils, mechanisms governing the acidification, modeling acidification in space and time, producing maps of soil acidification risk), (2) measurement of acidity (including spatial and temporal variability on the micro- and macroscale), (3) growth-inhibiting factors associated with acids soils (e.g., ion toxicity, nutrient deficiency), and (4) management of acidification and acidity in agriculture and forestry, including aspects of chemical amelioration of soils, growing resistant plants, and adapted farming systems, and finishing with the role of pH in phytoremediation of metal-contaminated soils. Therefore, in

comprehensively characterizing the role of soil acidity and its amelioration in soil fertility, health, and productivity, the book covers a wide range of topics that genuinely span such scientific disciplines as agronomy, forestry, soil science, plant biology, breeding, ecology, modeling, land rehabilitation, and conservation.

All chapters have been reviewed according to the standard of high-impact international journals. I would like to thank the contributors, who patiently went through a number of revisions of their chapters. I would also like to thank the Marcel Dekker, Inc., staff for capable handling of numerous issues and for their dedication to producing a high-quality multidisciplinary book.

Zdenko (Zed) Rengel

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Soil Acidification: The World Story

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1   INTRODUCTION

For decades, soil acidity has been a major constraint to crop production throughout the world. However, in developed nations, the use of lime to counteract acidity in high-input agriculture over the past 50 to 100 years has led to a marked decrease in the area of acid soils under cultivation and to spectacular increases in yields. Still, in the case of deep naturally acid profiles, little amelioration of subsoil acidity has occurred, and in some cases (e.g., in Australia), neutral to alkaline subsoils have actually been acidified as a result of the failure to correct topsoil acidity [1]. In contrast, in developing nations with largely low-input agriculture and farmers able to afford only minimal applications of lime, very little amelioration of soil acidity has taken place. In fact, the condition has probably worsened in many areas.

Experimental results [2] show that counteracting subsoil acidity can result in substantial (20–100%) yield responses, particularly under rain-fed conditions. There are a number of reasons for this situation. Many soils in developing nations are naturally very acid and infertile to great depths in the profile. Cultivation of such soils without inputs results in very low yields, which has maintained the farming population in poverty. As a result, farming has mined what little resources

the soils have had to offer and yields have tended to decrease rather than increase with time for lack of adequate inputs.

Without access to financial loans to facilitate the purchase of inputs, it is extremely difficult for these resource-poor farmers to break out of this cycle of poverty. The small loans required by such farmers are seldom available from traditional lending institutions. Despite the results of several years of research which have shown that yields can be more than doubled by the application of lime to acid soils, this practice has not been widely adopted in developing nations because of the unavailability or high cost of lime, the lack of access to loans, and poor infrastructure capacity.

Poor crop growth on acid soils is usually a direct result of aluminum toxicity. When soil pH_{H2O} drops below 5, aluminum becomes soluble and causes severe root pruning that results in reduced water and nutrient uptake (see Chapter 10). Thus, one of the first manifestations of the harmful effects of soil acidity is drought stress. Many of the acid soils in developing nations are deep and well drained and have high yield potentials if the roots could penetrate and extract water from the acid subsoils, normally beyond their reach [3]. The limiting factors associated with poor root penetration are the lack of Ca^{2+} and/or excess Al^{3+}. The efficient use of subsoil water again requires inputs such as gypsum and lime, which have been shown to promote yields on soils with acid highly weathered subsoils throughout the world [4]. A simple test is available to identify subsoils likely to respond to gypsum [3]. Thus, the solution to the problem of soil acidity in developing nations does not require more research but rather an aggressive extension program to promote the use of lime, gypsum, and other inputs (phosphorus, nitrogen, potassium, etc.) whose benefits have been amply demonstrated. This should be coupled with an appropriate system for making small production loans to farmers [5]. It is often not appreciated that soil acidification is a severe degradation process. Consequently, its remediation should be seen as a capital cost, which can be amortized over a number of years.

2 AREAL EXTENT OF ACID SOILS

Estimates of the total area of topsoils affected by acidity throughout the world vary from 3.777×10^9 [6] to 3.950×10^9 [7] ha, representing approximately 30% of the total ice-free land area of the world. The distribution of acid soils by region in relation to cultivated and total ice-free land area is presented in Table 1. The largest areas of acid soils are in South America, North America, Asia, and Africa. In most regions, the area of acid soils far exceeds the area under cultivation, indicating that large areas of acid soils are still under natural forest or grassland vegetation. The total area affected by subsoil acidity is estimated as 2.918×10^9 ha [6], meaning that approximately 75% of the acid soils of the world suffer from subsoil limitations due to acidity.

TABLE 1 Areal Extent of Acid Soils in Relation to Total Ice-Free Land Surface and Area Under Cultivation for the Regions of the World

| | | | Australia/ New Zealand | Europe | Asia | | | | America | | |
	World	Africa			Near East	Far East	Southeast and Pacific	North and Central	North	Central	South
Acid land ($\times 10^9$ ha)	3.950	0.659	0.239	0.391	0.005	0.212	0.314	0.512	0.662	0.036	0.916
Total land ($\times 10^9$ ha)	13.15	3.01	0.82	0.48	0.50	1.48	0.40	0.85	2.11	0.10	1.75
Acid/total (%)	30	22	30	37	1	12	63	57	30	35	52
Cultivated land ($\times 10^9$ ha)	1.4	0.158	0.032	0.154			0.519		0.239		0.077
Cultivated/ total (%)	10.6	5.2	3.9	32.1			18.9		11.3		4.4

Source: Data from Ref. 7.

Using a scale for acid intensity based on pH_{H2O} ranges of <3.5 (extreme), 3.5–4.5 (high), 4.5–5.5 (moderate), and 5.5–6.5 (slight), the global distribution of these acid topsoils and subsoils is depicted in Figs. 1 and 2. Areas associated with each of these subdivisions are tabulated by region in Table 2. On a global basis, only a relatively small proportion of acid topsoils fall in the extremely acid category, with South America accounting for the lion's share. The remaining acid soils are fairly evenly distributed among the other categories. Except for the extremely acid category, a similar pattern is exhibited for subsoils. In the Americas, Africa, and Asia, a large proportion of soils with topsoil acidity also exhibit marked subsoil acidity of similar intensity, indicating the strong linkage between top- and subsoil acidity under pristine conditions. Because Al^{3+} becomes soluble and toxic below pH $\sim$ 5.0 to 5.2, the categories of moderate and high acidity are of particular interest in agronomic terms, accounting for 67 and 79% of the world's acid topsoils and subsoils, respectively.

In Tables 3 and 4, the areal extent of acid topsoils has been broken down according to the Food and Agriculture Organization (FAO) Soil Groups [8] and Soil Taxonomy [9] Orders. As one would expect, the largest areas of acid soils occur in Soil Groups that have been either intensely weathered [Acrisols, Nitosols, Ferralsols] (Ultisols, Oxisols) or formed on basic cation-poor parent materials [Podzols, Histosols, Arenosols, Podzoluvisols, Cambisols] (Entisols, Spodosols, Inceptisols, Histosols).

The preceding estimates (Tables 1–4) should be treated with some caution as they are derived from databases that contain significant omissions, possibly inappropriate extrapolations and assumptions, and unspecified methods of measuring pH and have not been georeferenced [6]. However, they are the best estimates available at present.

3 TYPES OF ACID SOILS

3.1 Naturally Occurring Acid Soils

3.1.1 Due to Intensive Weathering

The natural weathering processes for acid soils involve leaching of the parent material by acidic rain due to the presence of H_2CO_3 that provides protons and removes basic cations in the leachate. As a result, parent rocks weather to form acid soils with the rate of acidification depending on the nature of the parent material, effective rainfall, and temperature. Highly basic parent materials weather more rapidly than highly siliceous substrates, with both increased rainfall and temperature promoting the process. Under extreme conditions such as occur in the humid tropics, most silicate minerals in the parent material are weathered away by desilication, leaving little other than the oxides of iron and aluminum. Such soils (Oxisols and Ultisols) are usually weathered to great depths. Thus, in nature, one finds
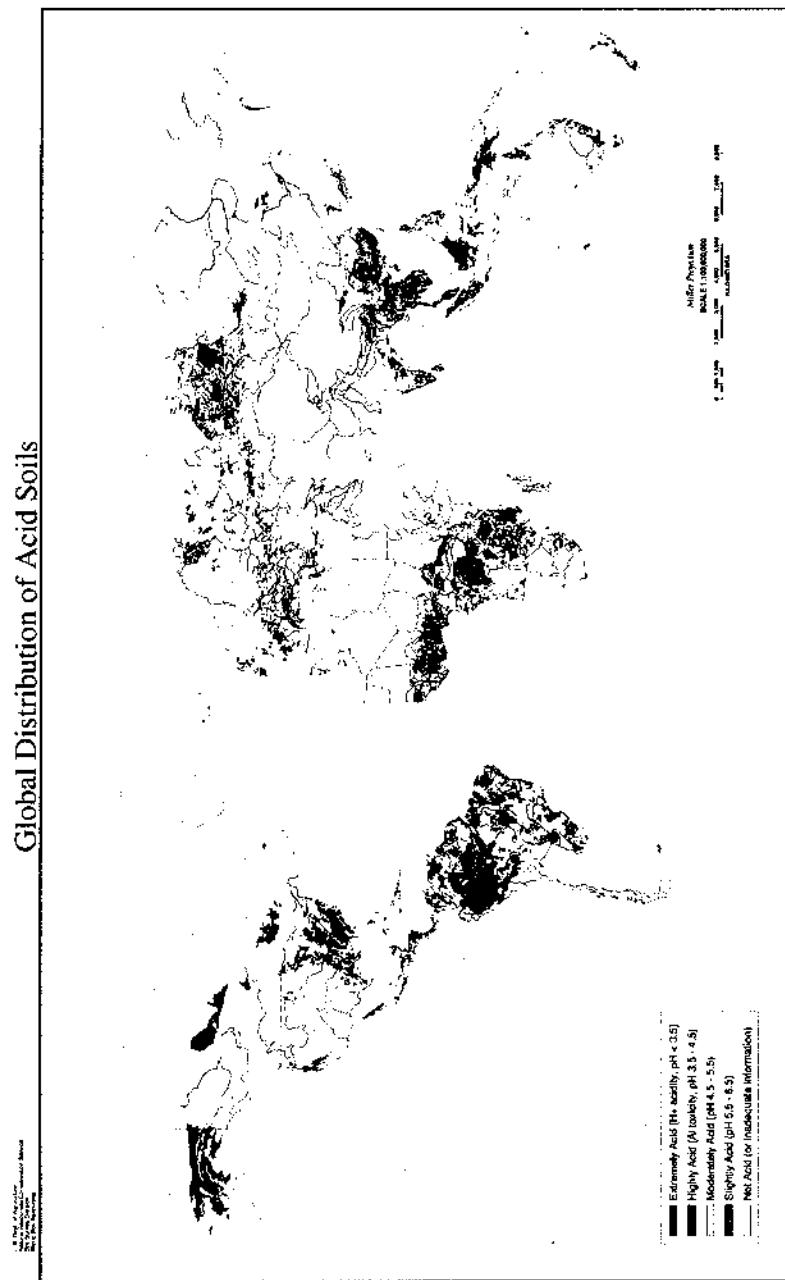
FIGURE 1 Global distribution of soils with acid topsoils. (Reprinted with permission. Copyright Courtesy Natural Resource Conservation Service, USDA, USA.)
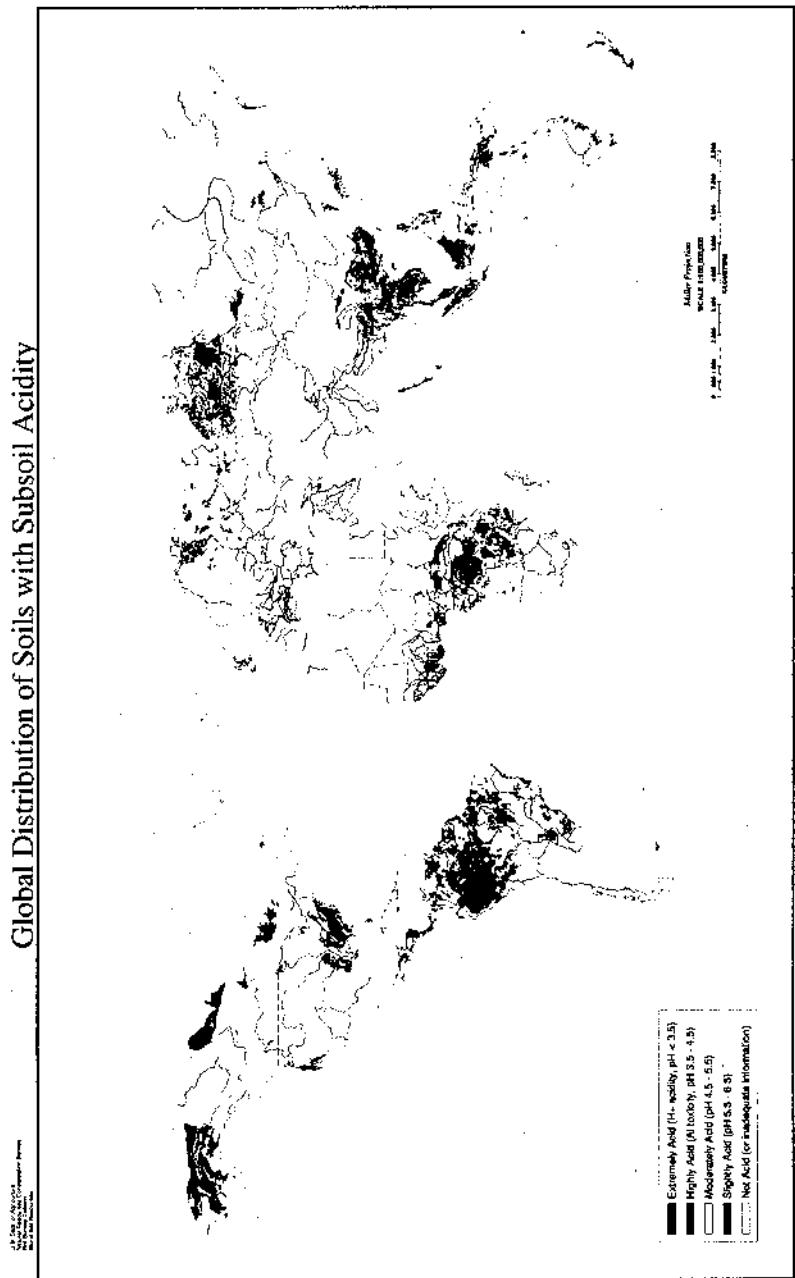
FIGURE 2 Global distribution of soils with acid subsoils. (Reprinted with permission. Courtesy Natural Resource Conservation Service, USDA, USA.)

TABLE 2 Areal Extent ($\times 10^9$ ha) of Acid Topsoils and Subsoils of Varying Intensity for Various Regions of the World

Class	World		America North		America South		Africa		South and East Asia		Europe	
	Top	Sub	Top	Sub	Top	Sub	Top	Sub	Top	Sub	Top	Sub
Slight (pH_{H2O} 5.5–6.5)	1.25	0.58	0.21	0.11	0.25	0.12	0.43	0.18	0.17	0.08	0.00	0.00
Moderate (pH_{H2O} 4.5–5.5)	1.54	1.38	0.30	0.28	0.44	0.42	0.33	0.29	0.19	0.15	0.05	0.11
High (pH_{H2O} 3.5–4.5)	0.98	0.95	0.09	0.09	0.36	0.36	0.12	0.12	0.32	0.30	0.13	0.01
Extremely acid ($pH_{H2O} < 3.5$)	0.15	0.01	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Total	3.78	2.92	0.60	0.49	1.18	0.90	0.88	0.60	0.69	0.54	0.20	0.13

Source: Data from Ref. 6.

TABLE 3 Areal Extent ($\times 10^6$ ha) of Acid Topsoils for the FAO Soil Groups

Soil Group	World	Africa	Australia and New Zealand	Near East	Europe	Asia Far East	Asia Southeast and Pacific	Asia North and Central	America North	America Central	America South
Fluvisols	50	13	0	NA	1	5	19	6	0	1	5
Gleysols	402	57	1	NA	27	6	19	136	84	2	71
Regosols	293	26	97	NA	6	5	1	52	93	1	11
Arenosols	280	101	83	2	NA	0	5	NA	NA	0	88
Rankers	61	1	0	3	18	26	4	1	NA	NA	8
Andosols	34	1	2	NA	1	1	3		7	6	14
Cambisols	300	26	12	0	59	21	45	28	68	6	35
Podzoluvisols	255	NA	NA	NA	75	8	0	168	4	NA	NA
Podzols	415	11	11	NA	146	1	4	23	209	0	8
Planosols	15	0	8	NA	2	NA	1	NA	2	1	0
Acrisols	731	86	12	0	3	126	164	NA	94	13	233
Nitosols	118	60	2	NA	NA	7	16	NA	8	4	20
Ferralsols	727	278	9	NA	0	0	16	NA	0	1	422
Histosols	270	NA	1	NA	54	8	17	97	91	1	NA
Total	3950	659	239	5	391	212	315	512	662	37	916

Source: Data from Ref. 7.

TABLE 4 Aerial Extent ($\times 10^9$ ha) of Acid
Topsoils for Soil Taxonomy Orders

	Order	
Order	Area	%
Entisols	0.824	20.9
Inceptisols	0.561	14.2
Andisols	0.034	0.9
Spodosols	0.415	10.5
Alfisols	0.255	6.5
Ultisols	0.864	21.8
Oxisols	0.727	18.4
Histosols	0.270	6.8

Source: Adapted from Ref. 7.

a range of soils in different stages of weathering exhibiting different degrees of acidity often reflected in the systems used to classify soils.

In terms of soil taxonomy [9], acid soils in this category fall mainly into four Soil Orders, namely Oxisols (Ferralsols), Ultisols (Acrisols, Nitosols, Planosols), Andisols (Andosols), and Alfisols (Podzoluvisols). The nearest FAO Soil Group equivalents have been placed in parentheses. Some highly acid soils (acid sulfate) also occur in the Inceptisol Order.

Oxisols are the most highly weathered but not necessarily the most acidic soils (Table 5) because, in the final stages of weathering, soil pH increases due to the high point of zero charge ($>$pH 7) of Fe and Al oxides. They have very low basic cation status and effective cation exchange capacity (ECEC), but exhibit appreciable variable charge indicated by the difference [cation exchange capacity (CEC) $-$ ECEC]. In this context, CEC refers to the value obtained with 1 M NH_4OAc (pH 7), and ECEC is the sum of exchangeable cations ($Al^{3+} + Ca^{2+} + Mg^{2+} + K^+ + Na^+$). Often they are heavy textured with a more or less uniform distribution of clay with depth. They are extremely poor in available phosphorus but usually have adequate to excellent physical properties.

Ultisols are less highly weathered but often more acid than Oxisols and usually contain appreciable amounts of silicate clay minerals (mainly kaolinite). Clay content increases with depth often abruptly, giving rise to a Bt horizon. In general, their ECEC values are higher than for Oxisols but they also exhibit considerable variable charge. They contain appreciable levels of toxic exchangeable aluminum to depth associated with low basic cation status (Table 5). Unfortunately, the NRCS-USDA database [13] does not contain information on exchangeable Al^{3+} and, consequently, many values are missing in Table 5.

TABLE 5 Chemical Properties of Representative Oxisols, Ultisols, Andisols, and Alfisols

Depth (m) (horizon)	pH H$_2$O	pH KCl	OC (g kg^{-1})	Clay (%)	Exchangeable cations (cmol$_c$ kg^{-1})					
					Ca	Mg	K	Al	CEC pH 7	ECEC
Oxisol (Aquic Hapludox) [10]										
0–02		4.5	14	39.9	3.7	1.6	0.32	0.3		5.92
0.3–0.5		4.0	9	42.1	0.8	0.4	0.13	2.1		3.43
0.6–0.8		4.1	3	45.3	0.3	0.4	0.10	2.9		3.70
Oxisol [11]										
0–0.2	5.0		7	59.0	2.8	1.4	0.25	0.6	6.7[a]	5.05
0.3–0.6	4.8		4	55.0	0.4	0.3	0.08	1.0	3.2	1.78
0.6–0.9	4.7		2	53.0	0.1	0.2	0.05	1.2	2.7	1.55
Ultisol (clayey, kaolinitic, isothermic Humic Hapludult) [12]										
0–0.3 (Ap)	4.4	4.0	20	23.0	0.50	0.03	0.31	2.7	11.9	3.54
0.3–0.6 (Bt1)	4.3	3.7	8	40.2	0.50	0.05	0.15	3.9	13.1	4.60
0.6–1.1 (Bt2)	4.4	3.5	3	40.7	0.63	0.08	0.03	2.6	9.2	3.34
Ultisol (fine, parasesquic, mesix Xeric Haplohumult) [13]										
0–0.1 (A1)	5.1		52	54.2	12.1	3.8	1.1		27.5	
0.2–0.4 (B1)	4.7		11	65.0	4.6	2.4	0.2		17.1	
0.8–1.2 (B31)	4.4		5	79.0	1.7	1.5	0.1		13.6	

Andisol (medial, isothermic Acrudoxic Hapludand) [12]									
0–0.3 (A1)	4.7	4.6	42	0.55	0.09	0.06	1.20	26.8	1.90
0.3–0.6 (Bw1)	4.6	4.8	15	0.50	0.08	0.07	0.30	29.5	0.95
0.9–1.9 (Bw3)	4.3	5.0	5	0.50	0.03	0.03	0.50	26.9	1.06
Andisol (Histic Duraquand) [13]									
0–0.2 (A1)	4.7	5.8	106	5.7	0.6	0.6		48.6	
0.2–0.4 (A2)	5.0	1.3	68	0.8	0.2	0.2		42.7	
0.4–0.6 (Bw)	5.7	3.3	39	0.2	0.1	0.1		28.2	
Alfisol (fine-silty, mixed, mesic Typic Endoaqualf) [13]									
0–0.1 (A1)	5.3	16.9	18	6.2	1.8	0.8		12.1	
0.3–0.4 (B1t)	5.1	26.9	3	9.4	3.6	0.7		16.4	
0.6–0.8 (B21t)	5.5	34.1	3	16.0	8.6	0.9		26.4	
Alfisol (fine-loamy, siliceous, semiactive, thermic Typic Paleudalf) [13]									
0–01 (Ap)	5.2	21.7		1.6	1.3	0.3		6.0	
0.1–0.8 (B21t)	5.2								
0.8–1.1 (B22t)	5.2	23.2		1.1	1.4	0.3		5.4	

a At pH 6.0.

Andisols, which are most commonly not very acidic, are dominated by amorphous minerals (allophane and imogolite), organic matter, and variable charge. They have very high contents of organic matter in the surface horizon, with good to excellent physical properties down the profile. The acidic Andisols are found mainly in hot, humid regions and can become quite acid, with low basic cation content (Acrudoxic Hapludand) (Table 5).

In contrast to Ultisols, Alfisols are much less highly weathered, with only some being acidic. They usually exhibit increasing silicate clay content (mainly 2:1 clay minerals), basic cation status, and pH with depth. In Australia, many naturally nonacidic Alfisols have become acidic as a result of anthropogenic sources of acidity (see Chapters 4 and 5).

3.1.2   Acid Sulfate Soils

These soils, which cover 24 million ha worldwide, usually fall in the Inceptisol (Gleysols, Rankers, Cambisols) and Entisol (Fluvisols, Gleysols, Regosols, Arenosols) Orders and are found mostly in the delta areas of the great rivers. Prior to drainage, they have a neutral reaction as unripe sulfidic clays, but they become extremely acidic when drained (raw acid sulfate soils) due to the oxidation of reduced sulfur compounds (FeS_x) to sulfuric acid. After complete oxidation of the S compounds and dissipation of the sulfuric acid, which often contaminates adjacent water bodies, sulfate soils remain strongly acid (ripe acid sulfate soils). Both raw and ripe varieties contain high levels of exchangeable Al^{3+} (dissolved by the acid) and high basic cation status (from their riverine origin). An example of a ripe acid sulfate soil (Typic Sulfaquept) is presented in Table 6. The pH of acid sulfate often decreases with depth, reflecting the stronger oxidizing conditions near the surface. Texture is variable, depending on the nature of the alluvial parent material. The intensity and extent of the acidity produced can be controlled by manipulation of the water table.

3.1.3   From Parent Materials Poor in Basic Cations

These soils occur in the Spodosol (Podzols), Histosol (Histosols), and Entisol (Fluvisols, Gleysols, Regosols, Arenosols) Orders and are usually derived from organic, siliceous or basic cation–poor organic parent materials (Table 7).

Spodosols occur mainly in temperate regions on extremely basic cation–poor, unbuffered, coarse-textured parent materials. The spodic horizon (Bh) forms as a result of the translocation of basic cations, iron, and organic matter from the surface horizons, which, as a result, become extremely acid.

Histosols, which have very high organic matter contents, are usually acidic to strongly acidic depending on inputs of basic cations from surrounding mineral soils. They have very high CEC values due to the highly charged nature of organic matter. The acidity is due mainly to the H^+ ions, with the Al^{3+} ions making up

TABLE 6 Chemical Properties of Representative Inceptisols

Depth (m) (Horizon)	pH H$_2$O	pH KCl	OC (g kg^{-1})	Clay (%)	Exchangeable cations (cmol$_c$ kg^{-1})						
					Ca	Mg	K	Na	Al	CEC pH 7	ECEC
Inceptisol (sandy-skeletal, mixed, mesic Typic Dystrochrept) [13]											
0–01 (A1)	4.1	2.8	55	3.0	1.1	0.6	0.2				2.0
0.2–0.5 (B22)	5.1	3.2	7	2.3	0.1	0.2	0.0				0.3
0.5–0.7 (B23)	5.2	2.8	2	1.8	0.2	0.1	0.0				0.3
Inceptisol (Typic Sulfaquept) [14]											
0–0.05	2.9	2.8	78		0.7	4.4	0.2	3.7	18.3		27.3
0.15–0.25	3.5	3.2	73		0.1	2.6	0.2	2.6	15.3		20.8
0.35–0.45	3.2	2.8	13		0.2	3.0	0.2	1.8	13.1		18.3

TABLE 7 Chemical Properties of Representative Spodosols, Histosols, and Entisols

Depth (m) (Horizon)	pH H2O	PH KCl	OC (g kg⁻¹)	Clay (%)	Exchangeable cations (cmol_c kg⁻¹) Ca	Mg	K	Na	CEC pH 7	ECEC
Spodosol (sandy, siliceous, isohyperthermic Grossarenic Entic Haplohumod) [13]										
0–0.2 (A11)	4.0	3.5		28.8	0.1	0.3	0.1	0.0	0.4	
1.0–1.5 (A24)	4.3	3.8	0	29.2	0.1	0.0	0.0	0.0	0.1	
1.7–1.9 (B12h)	4.5	3.7	5	38.3	0.4	0.2	0.1	0.0	3.3	
Spodosol (sandy, siliceous, thermic Aeric Alaquod) [13]										
0–0.2 (A)	3.4		58	0.4	0.4	1.0	0.2	0.0	16.6	
0.2–0.2 (E)	3.9		3	0.4	0.0	0.0	0.0	0.1	1.1	
0.3–0.4 (Bh)	4.0		26	3.4	0.1	0.0	0.0	0.1	12.4	
Histosol (Dysic Typic Cryohemist) [13]										
0–0/2 (OiL31)	3.9		475		19.1	6.4	3.0	1.0	95.5	29.5
0.2–0.5 (OAL32)	4.6		476		53.1	12.5	0.7	0.9	149.9	67.2
0.5–1.3 (OA233)	4.2		449		29.4	9.3	0.4	0.8	160.5	39.9
Histosol (very-fine, mixed, evic, isohyperthermic Terric Troposaprist) [13]										
0–0.1 (OA1)	5.5	4.7		39.8	20.9	7.2	1.2	2.2	69.8	31.5
0.1–0.4 (OA2)	5.0	4.4		14.9	4.1	2.5	0.0	0.5	36.6	22.0
0.4–0.8 (OA3)	5.1	4.7		15.8	3.8	2.5	0.0	0.5	31.9	22.6
Entisol (mesic, uncoated Typic Quartzipsamment) [13]										
0.01 (A1/B1)	3.4		17	2.0	0.2	0.2	0.2			
0.2–0.5 (B23)	4.3	4.4	2	6.3	0.0	0.0	0.1			
0.5–0.7 (B24v)	4.4	4.3	1	3.9	0.0	0.1	0.1			
Entisol (sandy-skeletal, mixed, mesic, Typic Udorthent) [13]										
0–0.2 (Ap)	5.0	4.3	28	5.1	1.6	0.1	0.2			
0.3–0.4 (B22)	5.3	4.6	6	2.6	0.0	0.0	0.0			
0.6–0.9 (2C2)	5.7	4.8	1	1.2	0.2	0.0	0.2			

only a small proportion of the acidity in most Histosols. Some Histosols in fens (unforested) and swamps (forested) can have pH_{H2O} values in the neutral range (6–7.5). Entisols are coarse-textured soils that become acid during weathering due to the lack of buffering capacity (very low CEC) within the soil.

3.2 Anthropogenically Derived Acid Soils

3.2.1 From Acid Deposition

Combustion of fossil fuels over the past two centuries has acidified rainfall with sulfuric and nitric acids in many areas of the world (see Chapter 4). In addition, NH_x from livestock and industrial sources can have a marked effect on topsoil acidification when the ammoniacal nitrogen after deposition is oxidized to nitrate, which is then leached from the topsoil [15]. There is also evidence that volcanic emissions of SO_2 and HCl can contribute to acid precipitation [16].

Long-term acid deposition can have negative impacts on soils, particularly in pristine systems, such as forests, where opportunities for amelioration are minimal. This is particularly true when the atmospheric load of NH_x, H_2SO_4, or HNO_3 saturates or exceeds the demand of the ecosystem for N, which can cause changes in species diversity. For example, Sverdrup et al. [17] showed that 81% of Swedish forests are receiving greater than critical acid loads, which are projected to cause growth losses of 19% of current levels. Edges of forests are particularly vulnerable as they tend to filter off preferentially atmospheric NH_x from such sources as livestock production. In Belgium, De Schrijver et al. [15] found that soil pH_{H2O} at the edge of a Corsican pine stand downwind from an intensive livestock area was 3.1, whereas in the center of the stand it was 3.8. The edge received twice as much NH_4-N as the center. In cultivated soils, such negative impacts can be readily counteracted by liming, a common agronomic practice (see Chapter 11).

Severe forest decline due to acid rain has been reported in Europe and North America on coarse-textured, poorly buffered soils where basic cation depletion and acidification can be severe. Acid depositions of 0.8–6.4 kmol H^+ ha^{-1} $year^{-1}$ have been recorded in central Europe [18]. At Rothamsted over the period 1883–1983, a soil in the wilderness area (regenerated hardwood forest), which has been unlimed and unfertilized since 1885, has become severely acidified (Table 8) as a result of acid deposition rates estimated to be 1.05, 1.67 and 3.90 kmol H^+ ha^{-1} $year^{-1}$ in 1850, 1920–1930, and 1983, respectively. Johnston et al. [19] estimated that this acidification resulted in basic cation losses equivalent to 14.0, 9.0, and 5.5 $kmol_c$ Ca^{2+} ha^{-1} $year^{-1}$ in 1883, 1930, and 1984, respectively. Such losses can severely reduce the fertility status of the soil, subjecting the trees to nutritional stress. On the other hand, Markewitz et al. [20] in North Carolina found that acid rain accounted for only 38% of soil acidification over a 30-year period. Although tree species can contribute to forest soil

TABLE 8   Change in pH_{H2O} Value with Depth on an Unlimed and Unfertilized Soil Under Woodland (Mainly Regenerated Deciduous Species) at Rothamsted over the Period 1883–1983

	Sampling date			
Depth (m)	1883	1904	1965	1983
0–0.23	7.1	6.1	4.5	4.2
0.23–0.46	7.1	6.9	5.5	4.6
0.46–0.69	7.1	7.1	6.2	5.7

Source: Adapted from Ref. 19.

acidification, the magnitude is small compared with that of acid deposition [15] and other factors [21].

3.2.2   From Intensively Managed Row Crop Agriculture

Under intensive agronomic row crop production, the major acidifying acid input is usually ammoniacal fertilizer N, which can rapidly acidify a soil profile if lime applications are not made. Disturbance of the C cycle and removal of alkaline products can also contribute. The acidity from ammoniacal fertilizers arises from the nitrification reaction, with the quantity of acidity produced depending on N source, extent of nitrate leaching, and uptake of N by the crop (see Chapters 2 and 3). For example, annual applications of 300 kg N ha^{-1} as urea to two crops of corn per year over 18 years caused severe acidification of an Ultisol in Nigeria [22,23] (Table 9). In addition to a substantial loss of organic C (OC), the profile has been depleted in basic cations and, with decreasing pH, increasing amounts of exchangeable Al^{3+} and Mn^{2+} (data not presented) have appeared in both top- and subsoils. High concentrations of Al^{3+} and Mn^{2+} are toxic to the crop, with Al^{3+} impairing root growth and Mn^{2+} having adverse effects on the tops. Retaining the corn residue has had a slight positive effect in stemming acidification. The type of ammoniacal source also has an effect on the rate of acidification, with ammonium sulfate having a greater acidifying effect than urea or calcium ammonium nitrate [24]. Similar results were obtained by Bouman et al. [25] in Saskatchewan, except that Mn^{2+} rather than Al^{3+} became soluble and was likely to be the main toxicant when soils were acidified by excessive fertilization.

3.2.3   From Pasture Systems

For pastures to be productive, inputs of nitrogen (and other fertilizers) are required, which often leads to acidification, the intensity of which depends on the nitrogen

TABLE 9 Effect of 18 Years of Continuous Corn Cultivation (Two Crops/Year) on Soil Chemical Properties of a Nigerian Alfisol (Clayey, Kaolinitic, Isohyperthermic Oxic Kandiustalf)

Treatment	Depth (m)	pH H$_2$O	OC (g kg^{-1})	Exchangeable cations (cmol$_c$ kg^{-1})					
				Ca	Mg	K	Al	H	ECEC
Bush fallow (control)	0–0.1	6.2	19	11.2	1.5	0.7	0.1	0.0	13.5
	0.1–0.2	6.2	6	4.7	1.0	0.4	0.1	0.0	6.2
Corn (residue removed)	0–0.1	4.5	6	1.9	0.4	0.2	0.7	0.3	3.5
	0.1–0.2	4.5	5	2.1	0.5	0.1	0.9	0.3	3.9
Corn (residue retained)	0–0.1	4.8	10	3.6	0.7	0.3	0.4	0.2	5.2
	0.1–0.2	4.7	6	3.0	0.5	0.2	0.5	0.4	4.6

Source: Adapted from Ref. 22.

carrier and rate of application. Long-term (1876–1984) applications of ammoniacal fertilizers to pasture systems clearly acidify the soils as demonstrated by the work of Johnston et al. [19] at Rothamsted (Table 10). On the control plot (no fertilizer) and no-nitrogen plots (received other fertilizers), soil pH remained fairly constant, with the slight increase between 1856 and 1923 being due to small applications of chalk (lime) between 1881 and 1896. There was a slight downward drift

TABLE 10 Change in Soil pH with Time Due to Varying Annual Rates of Ammonium Sulfate Application on the Park Grass Experiment That Started at Rothamsted in 1856 at an Estimated pH$_{H2O}$ of 5.6 to 5.8.

Nitrogen rate (kg N ha^{-1} year^{-1})	Depth (m)	Sampling date				
		1876	1923	1959	1976	1984
0	0–0.23	5.3	5.7	5.2	5.3	5.0
	0.23–0.46	6.1	6.2	5.3		5.7
48	0–0.23	5.3	4.8	4.0	4.1	3.7
	0.23–0.46	6.2	6.2	5.2		5.1
96	0–0.23	4.8	4.0	3.8	3.9	3.6
	0.23–0.46	6.4	4.8	4.3		4.1
145	0–0.23	4.3	3.8	3.7	3.7	3.4
	0.23–0.46	6.5	4.4	4.1		4.0

Source: Data from Ref. 19.

of topsoil pH after 1923, due largely to atmospheric depositions estimated to be about 2 kmol H^+ ha^{-1} year^{-1} from the 1920s to 1984. This is also reflected in subsoil pH. On the plots receiving ammonium sulfate, there was an initial rapid decline in top- and subsoil pH, which then leveled out to an equilibrium value of about 3.6 ± 0.2 in the topsoil, with the subsoil being slightly less acid. This equilibrium topsoil pH was reached in about 50 years on the high-N treatments, whereas 100 years was required on the low-N treatments. Buffering in this soil is the result of the dissolution of Al^{3+} from aluminous minerals. Based on estimates of other acidifying processes (crop removal of basic cations and acid precipitation), the nitrification reaction and leaching of nitrate produced at least 90% of the acidity over this period. However, because nitrification is severely impeded by strong acidity, further acidification of the topsoil due to nitrification will now be minimal as shown by the lack of nitrate in the grass samples from the very acidic plots [26]. Under such conditions where atmospheric inputs constitute a large proportion of the H^+ entering the soil, any H^+ entering the system is likely to move straight through and continue to acidify the subsoil because of the lack of buffering by H^+–Ca^{2+} exchange. On the other hand, the pH value of treatments receiving nitrogen in the form of nitrate increased by 0.5 to 1.0 pH units (data not shown).
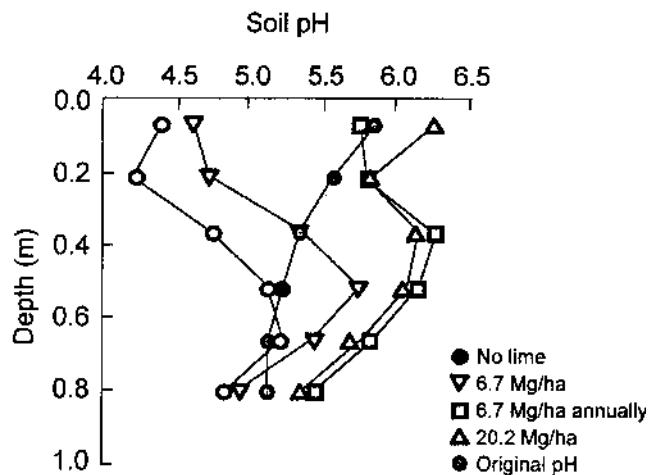
FIGURE 3 Effect of rates of calcitic limestone on soil profile acidity after 4 years under a Coastal bermudagrass (*Cynodon dactylon* [L.] Pers.) sod fertilized with NH$_4$NO$_3$ at an annual rate of 900 kg ha^{-1}. Single lime applications were made at the beginning of the experiment, except for the treatment labeled "6.7 t ha^{-1} annually." (From Ref. 27.)

In an experiment with Coastal bermudagrass fertilized with ammonium nitrate at a rate of 900 kg N ha^{-1} year^{-1} for 4 years, soil pH in the top 50 cm of soil declined markedly (Fig. 3) in the absence of lime. When sufficient lime was applied to neutralize the acidity produced and to form calcium nitrate, which can move into the subsoil, pH down the entire profile was increased due to the transfer of alkalinity from the top- to subsoil where roots assimilate more nitrate than calcium [3]. Thus, even in undisturbed pasture or grassland situations, it is possible to prevent acidification of the soil provided that adequate and timely applications of lime are made. What is important is that the topsoil should never be allowed to become acid, which requires regular applications of lime in the topsoil to neutralize the acidity.

Under grassland conditions, soil biota are very important in the cycling of nutrients. Acidification due to ammoniacal fertilizers can drastically reduce earthworm numbers and their biomass [28], resulting in the accumulation of thatch on the soil surface. Because of the lack of incorporation of these residues, decomposition and microbial mineralization are reduced.

4 RATES OF ACIDIFICATION

4.1 Pristine Systems

Johnson et al. [29] estimated the average net loss of Ca^{2+} from the floor of a forest in New York to be 60 mol$_c$ ha^{-1} year^{-1} during the period 1931 to 1984, which was much lower than more recently measured values (710 mol$_c$ ha^{-1} year^{-1} in O horizons and 322 mol$_c$ ha^{-1} year^{-1} in mineral horizons) in an adjacent forest from 1986 to 1990 (Table 11). They ascribed the differences to measured decreases in long-term trends in Ca^{2+} deposition from rainfall in recent decades, the reason for which is not known. In the O horizon, the main contributors to acidification of the forest floor were the production and leaching of sulfate and organic anions followed by uptake of basic cations. Removal of acids occurred by leaching of H^+ and Al^{3+} and by mineralization of organic matter. In the deeper mineral horizons, transfer of H^+ and Al^{3+} from the surface and uptake of basic cations were the main causes of acidification, while sulfate sorption and decomposition of organic anions consumed acidity.

In various parts of Europe, declines in soil pH have been recorded partially as a result of acid precipitation [30,31] and partially as a result of changes in vegetation or the redistribution of basic cations between underlying mineral soil and the organic O horizon [30]. Rates of acidification in Sweden have ranged from 0.3 to 0.9 pH units in 55 years [32], 0.5 to 1.0 pH units in 30–50 years [31], and 0.78 pH units in 35 years [33], and in Scottish forests Billet et al. [30] found decreases in pH in organic horizons of 0.07 to 1.28 and in mineral horizons of 0.16 to 0.54 over a period of 40 years.

TABLE 11 Acidification Caused by Various Factors in O Horizons and in Combined Mineral Horizons from a Spruce–Fir Forest in New York During the Period 1986–1990

Protons (mol$_c$ ha^{-1} year^{-1})	H$^+$	Al	NH$_4$	Basic cations	Mineralization	NO$_3$	SO$_4$	OA$^-$	Cl$^-$	Total
					O horizons					
H$^+$ produced	29		139	1117			1469	1318	69	4141
H$^+$ consumed		2061			1250	120				3431
Net										710
					Combined mineral horizons					
H$^+$ produced	631	1241	18	714	0					2604
H$^+$ consumed						39	903	1269	71	2282
Net										322

Source: Adapted from Ref. 29.

4.2 Managed Systems

Agricultural production systems undergo accelerated soil acidification as a consequence of anthropogenic inputs and outputs. In this respect, the rate at which a production system acidifies is a function of the intrinsic soil properties (buffering capacity), climate, and farming practice. As discussed previously, the resultant decline in soil pH associated with agricultural production systems may be sufficient to cause moderate to severe Al^{3+} and Mn^{2+} toxicity, thereby affecting the long-term economic viability of farming systems and resulting, in some cases, in permanent degradation of the resource base. It is, therefore, of importance that the rate of acid addition to soils by these various inputs and outputs be known in order to facilitate corrective actions by the producer and society as a whole.

Rates of acid addition in agronomic production systems have been compared with those in native ecosystems and found to be significantly higher [30,34]. Soil acidification rates can be estimated as either "absolute" changes or changes relative to some control soil. Using the first method, acid addition rates are calculated from analyses of soils before and after a period of acidification [35]. This requires comparable measurements, usually separated by many years [36]. However, relative rates of acidification can be derived from survey data (e.g., fence-line contrasts) and are reported more often because of the paucity of reference data from long-term studies. A compilation of acid addition rates under various cropping and pasture production systems is presented in Table 12. The values have invariably been derived using the model of Helyar and Porter [37] that takes into account changes in the size of various pools in the N and C cycles. Rates of acid addition range from net alkalization (25.2 to 20.5 kmol H^+ ha^{-1} $year^{-1}$) in the case of tobacco crops to significant acid additions (28 to 40 kmol H^+ ha^{-1} $year^{-1}$) in the case of banana plantations in the wet tropics (Table 12). In the former case, net alkalization is associated with approximately 70% of the nitrogen fertilizer being in the nitrate form because ammonium-based fertilizers cause the leaf to have poor curing properties [45]. In contrast, the extremely high acidification rates recorded in banana production systems are a consequence of fertigation with high rates of ammonium-based fertilizers (average application rate of 508 kg N ha^{-1} $year^{-1}$), coupled with the removal of significant alkalinity in both harvested product and plant pruning following bunch removal [45].

From a strategic perspective, quantification of acid addition rates under various agronomic production systems can assist producers, extension officers, and policy makers in making decisions on the long-term impact of a production system on the resource base. For example, the introduction of a legume species and its subsequent dominance in native pasture systems in northern Australia resulted in significant acidification to depth over a period of 15 years [39]. These grazing

TABLE 12 Estimated Acid Addition Rates (AARs) for a Range of Production Systems in Australia

Production system	AAR range (kmol H^+ ha^{-1} $year^{-1}$)	Comment	Reference
Agroforestry	0.9	Eucalypt forest compared with unimproved pasture	38
Grazed *Stylosanthes*-based extensive pasture	0–3.5	Legume-based extensive pasture production systems in the wet/dry tropics	39
Grazed clover pasture	1.2–3.6	Grazed white clover/paspalum grass pasture in the wet subtropics	40
Grazed clover pastures	0.8–4.4	Subterranean clover/annual or perennial grass pasture systems of the temperate highlands	39–44
Pasture cut for hay	1.0–6.0	Grass cut and removed without nitrogen fertilizer in the wet tropics	45
Pasture cut for hay	10.0–11.0	Nitrogen-fertilized grass pasture cut and removed for hay in the wet tropics	45, 46
Pasture cut for hay	0.6–1.0	Annual pasture grown under temperate conditions	47
Stylosanthes seed production systems	10.6	Irrigated seed production system in the dry tropics	39
Cereals	0.9–4.6	Continuous wheat with and without nitrogen fertilizers	48
Lupins	12.5	Continuous lupin monoculture (17 years) grown under a temperate climatic regime	48
Sugarcane	2.8–4.7	Sugarcane monocultures grown under a wet tropical and subtropical climate	45
Tobacco	−5.2 to −0.5	Tobacco monoculture grown under irrigation in the wet/dry tropics	41
Banana	28–40	Banana plantation crop in the wet tropics	41
Grapes	1.3–2.5	Vineyard in the subtropics	41

TABLE 12 *Continued.*

Production system	AAR range (kmol H^+ ha^{-1} $year^{-1}$)	Comment	Reference
Wheat/pasture rotation	0.2–5.1	Selected rotation studies of varying age	36, 43, 45
Wheat/lupin rotations	0.15–4.1	Rotations of varying age	43, 46–48
Cereal/clover pasture	0.15–0.92	Cereal/subclover pasture rotations under temperate climatic conditions	45, 48
Wheat/fallow rotation	−0.5–0.4	Wheat fallow rotation with no nitrogen applied	36
Irrigated rice/wheat/ pasture rotations	7.9–10.4	Rice/wheat/pasture grown under irrigation in a temperate environment	36

systems are characterized as low input and extensive in nature; consequently, conventional intervention strategies to ameliorate acidification through prophylactic applications of lime are uneconomic. Therefore, an alternative approach of identifying soils that are predisposed to accelerated acidification would assist land managers in making informed decisions on where to establish improved *Stylosanthes*-based native pastures. This has been done for an area in northern Queensland (the Dalrymple Shire) where a comprehensive land resource assessment had been undertaken [53]. Using intrinsic soil characteristics (silt, clay, and organic carbon content), a pedotransfer function was developed to predict pH buffer capacity [39]. By modifying the function of Helyar and Porter [37] and using a constant rate of net acid input (3.5 kmol H^+ ha^{-1} $year^{-1}$), the number of years for a soil association to fall from its current pH to 5.5 was estimated and depicted in a map using geographic information systems (GIS) technology (Fig. 4). Quite clearly, a significant proportion of the soils within the Dalrymple Shire are predisposed to accelerated soil acidification, and therefore the development of such risk maps would assist land managers in their decision-making process. By differentiating soils that are predisposed to accelerated acidification, a manager may strategically establish *Stylosanthes* in areas where the soils have the capacity to buffer acid inputs. In contrast, if managers do not have suitable areas of soils with high buffering capacity, they are aware of the risk of accelerated acidification and therefore may implement management strategies that minimize the risk of *Stylosanthes* dominance [39].
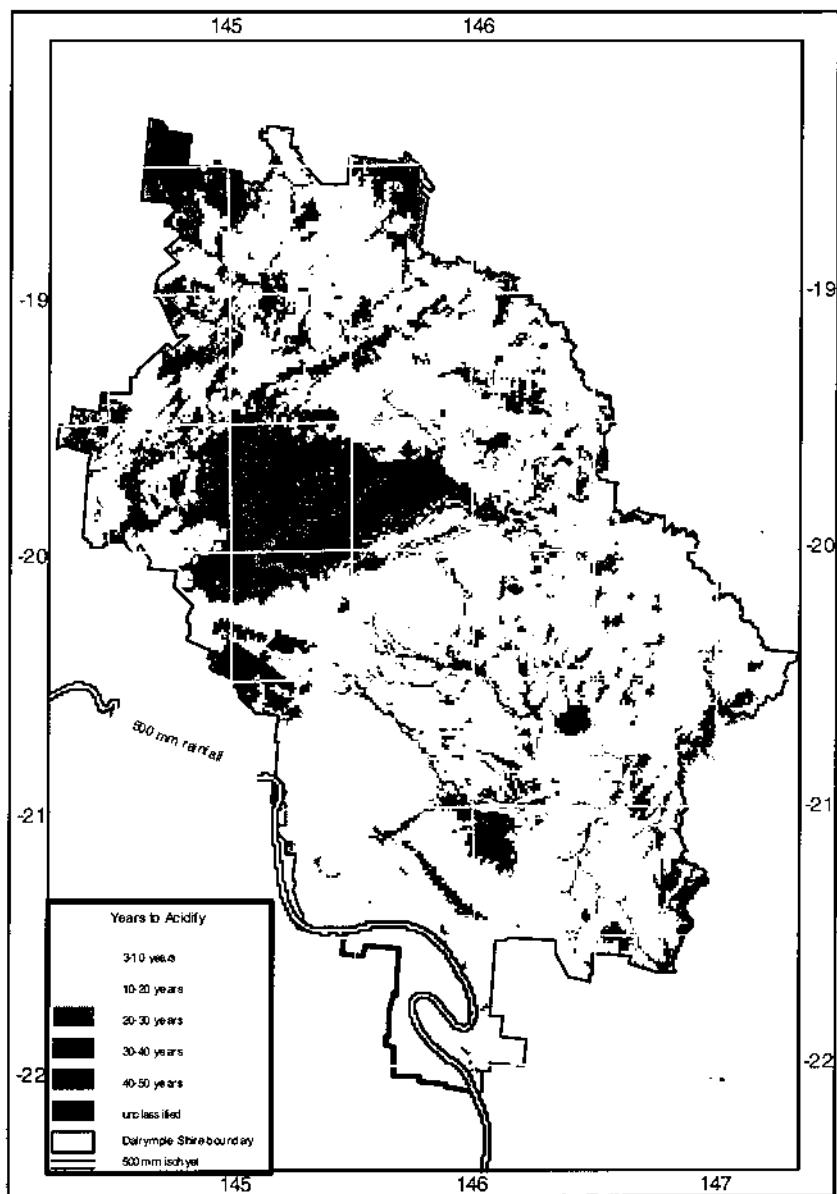
FIGURE 4 Acidification risk map for the Dalrymple Shire based on the time required for the soil pH_{H_2O} to decline to 5.5.

5 CONCLUSIONS

Topsoils affected by acidity account for 30% of the total ice-free area of the world with the Americas, Africa, and Asia accounting for the largest portions. Approximately 75% of these areas are also affected by subsoil acidity. As expected, intensely weathered soils (Oxisols and Ultisols) account for the largest areas but anthropogenic acidification resulting from the use of ammoniacal fertilizers and atmospheric fallout is of great importance in both cultivated and natural systems. Rates of acidification can vary from 0.7 kmol H^+ ha^{-1} $year^{-1}$ in pristine systems to as high as 40 kmol H^+ ha^{-1} $year^{-1}$ in production systems receiving high rates of ammoniacal N fertilizers.

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2

Role of Carbon, Nitrogen, and Sulfur Cycles in Soil Acidification

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1 INTRODUCTION

Under areas where rainfall exceeds evapotranspiration, soil acidification is an ongoing process that can be either accelerated by the activity of plants, animals, and humans or slowed down by careful management practices [1,2]. In areas that remain unaffected by industrial pollution, soil acidification is mainly caused by the release of protons (H^+) during the transformation and cycling of carbon (C), nitrogen (N), and sulfur (S) in the soil–plant–animal system [3,4]. Under managed systems much of the accelerated soil acidification is caused by increasing N and S inputs into the farming system (Table 1). For example, in areas of Australia where legumes have been grown continuously for more than 30 years, the soil pH has decreased by about one unit [5–10]. Similarly, in New Zealand, intensively managed legume-based dairy pastures require applications of approximately 2.5 tons of lime per ha every 6 years [11,12] to neutralize acidity mostly generated through loss of N from an accelerated N cycle.

Soil acidification caused by increases in C, N, and S input to a managed farming system can have adverse impacts where soils are unable to buffer against pH decrease. For example, in some parts of Australia, continuous legume cultivation and inappropriate nitrogenous fertilizer use have generated sufficient soil

TABLE 1 Contribution of C and N Cycles to Soil Acidification (Acidifications from Only C and N Cycles Were Considered in These Experiments)

Agricultural system	Total acidity (kmol H^+ ha^{-1} $year^{-1}$)	Percent contribution		References
		C cycle	N cycle	
Grazed pasture	3.46–4.22	49–60	41–51	1
Intensive dairy pasture	11.4	31	69	2
Hill country pasture	8.60	17	83	
Verano *Stylosanthes*	1.08	100	0	
Pasture				
Fertilized	1.42	65	35	
Unfertilized	0.16	100	0	
Leucaena-based pasture	1.03	84	16	8
Continuous wheat	0.35	98	2.0	10
1 Pasture–1 cereal rotation	0.41	19	81	
2 Pasture–1 cereal rotation	0.82	39	61	
Continuous pasture	0.92	25	75	
Hill country pasture	1.05–3.83	38–41	62–59	12
P trial—pasture	2.7–3.21	18–56	44–82	
Subclover	2.0	65	35	74
Phalaris	1.36	0.2	99	
Lupin	0.37	47	53	91
Lupin	0.19	—	100	
Lupin	0.47	38	62	
Cereal—annual pasture	0.19–0.23	100	0	96

acidity that wheat cultivation has had to be abandoned due to aluminum and manganese toxicity [13–15]. Soil acidification enhances the mobilization of toxic metals in soils, resulting in increased uptake by plants. Some of these toxic metals subsequently reach the food chain through plant products and grazing animals [16]. In this chapter, we first examine the various soil, plant, and animal processes that generate acid (protons; H^+ ions) during the cycling of C, N, and S. Second, the effects of these acid generation processes on soil acidification for legume-based pastures are examined. Third, methods to minimize soil acidification from C, N, and S cycles are proposed.

2 NUTRIENT CYCLING PROCESSES THAT GENERATE ACID OR ALKALI

The most significant proton (H^+) and hydroxyl ion (OH^-) generating processes occur during the cycling of C, N, and S (Table 2). In the case of the C cycle, dis-

solution of CO_2 to form carbonic acid in soil solution and synthesis and dissociation of carboxylic acids produced by plants and microorganisms are the two main sources of H^+ ions. The assimilation of CO_2 into carboxylic acids (including amino and fatty acids) in higher plants indirectly acidifies the soil explored by their roots. Dissociation of some newly synthesized organic acids creates negatively charged organates (e.g., $RCOO^-$) and H^+ ions. Charge-balancing basic cations from the rooting media are exchanged for the H^+ ions (see Sec. 2.1.1 for more details) to maintain both cytoplasmic pH buffering and internal plant charge balance. During plant senescence, organates (e.g., $RCOO^-$) are mineralized, generating HCO_3^- ions that neutralize protons. Storage of organic matter in soil or removal of plant products prevents the cycling being completed. Carbon commonly enters and leaves the terrestrial part of the C cycle as CO_2, particularly if growth and decomposition processes are in equilibrium. For ecosystems that have ap-

TABLE 2 Proton Generation and Consumption Processes in Carbon, Nitrogen, and Sulfur Cycles [12]

Process	Reaction equation	H^+ production $(\text{mol}_c \, \text{mol}^{-1})$
Carbon cycle		
Dissolution of carbon dioxide	$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$	+1
Synthesis of organic acid	$Organic\ C \rightarrow RCOOH \rightarrow RCOO^- + H^+$	+1
Nitrogen cycle		
N fixation	$N_2 + H_2O + 2R\text{—}OH \rightarrow 2R\text{—}NH_2 + 1.5\ O_2$	0
Mineralization of organic N	$RNH_2 + H^+ + H_2O \rightarrow R\text{—}OH + NH_4^+$	−1
Urea hydrolysis	$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2$	−1
Ammonium assimilation	$NH_4^+ + R\text{—}OH \rightarrow R\text{=}NH_2 + H_2O + H^+$	+1
Ammonia volatilization	$NH_4^+ + OH^- \rightarrow NH_3 \uparrow + H_2O$	+1
Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	+2
Nitrate assimilation	$NO_3^- + 8H^+ + 8e^- \rightarrow NH_3 + 2H_2O + OH^-$	−1
Denitrification	$2NO_3^- + 2H^+ \rightarrow N_2 + 2.5O_2 + H_2O$	−1
Sulfur cycle		
Mineralization of organic S	$Organic\ S + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$	+2
Assimilation of sulfate	$SO_4^{2-} + 8H^+ + 8e^- \rightarrow SH_2 + 2H_2O + 2OH^-$	−2
Oxidation of elemental sulfur	$2S° + 2H_2O + 3O_2 \rightarrow 2SO_4^{2-} + 4H^+$	+2

proached this steady state with respect to C-induced acid- and alkali-generating transformations, there is little net acidification caused by the C cycle.

In the case of the N and S cycles, mineralization and oxidation of organic N and S result in the production of H^+ ions. However, this is balanced by OH^- generated through uptake and assimilation of NO_3^--N and SO_4^{2-}-S by plants and microorganisms [17]. Leaching of SO_4^{2-} and NO_3^- with charge-balancing basic cations (Ca^{2+}, Mg^{2+}, K^+, or Na^+), rather than the H^+ ions generated during oxidation, results in permanent acidity remaining in the soil [18]. This is reflected in a decrease in pH in soils with low pH buffer power.

Commonly, the amount of S cycling within an ecosystem is roughly one tenth of the amount of N; in general, therefore, if the turnover time of S in a cycle is similar to that of N, N cycling will generate approximately 10 times the quantities of H^+ and OH^- ions generated during S cycling [19]. In addition, the extent of soil acidification resulting from a unit of N and S may differ due to differences in the form of element entering and leaving the system and the pathways involved. For example, N may enter a managed terrestrial ecosystem as N_2 gas, NH_4^+ in rainfall, or N fertilizer. It can leave as N_2, N_2O, NO_3^-, NH_3, or RNH_2 in products. As discussed later, N leaving in a form with more negative charge than the form of N entering the cycle acidifies the soil, whereas N leaving in a form with less negative charge than the form of N entering the cycle makes the soil more alkaline. In the former case, the charge balance in the soil is achieved through the release of H^+ ions, leading to soil acidification, whereas in the later case the charge balance is achieved through the release of OH^- or HCO_3^- ions, leading to soil alkalization. Sulfur in aerobic soils commonly enters as SO_4^{2-} in fertilizers and rainfall and leaves as SO_4^{2-} in drainage or RSH_2 in plant product, having little impact on the amount of acid it leaves in the soil. Difference in leaching of SO_4^{2-} and NO_3^- in the soil also contributes to the difference in the amount of acid produced by these two elements in soils. Some soils, particularly highly weathered soils, strongly adsorb SO_4^{2-} but not NO_3^-. Thus, SO_4^{2-} leaching is reduced [20] and the potential for greater recycling of S by plant uptake exists. In the case of NO_3^-, however, most soils have little ability to retain NO_3^-, making it susceptible to leaching [21–23]. Thus, NO_3^- leaching in legume systems (N input as N_2 gas) and ammonium-fertilized systems will leave the soil with permanent acidity. These aspects are covered subsequently in more detail.

We think it is easier to understand soil acidification if we break it into two parts: (1) biological processes that generate acid in soils and (2) processes that interrupt or uncouple nutrient cycling that leave acid in soils. The processes involved in the generation of H^+ and OH^- ions during C, N, and S cycling in soil can be grouped into two main categories: plant induced—the uptake and assimilation of C, N, and S; and soil induced—the transformation of C, N, and S in soil. These processes are discussed briefly in the following section.

2.1   Plant-Induced Processes

2.1.1   Carbon Assimilation

In higher plants, carbon is first assimilated as carbohydrates during the photosynthetic process. The subsequent metabolism of the photosynthates results in the synthesis of organic acids, such as malic and oxalic acids (process 4 in Fig. 1). At the cytoplasmic pH of the plants (pH ≈ 7.2 to 7.4), some of the carboxyl groups of simple acids, amino acids, proteins, and more complex structural carbohydrates (e.g., pectins) dissociate (processes 5 and 8 in Fig. 1) to produce H^+ ions [24].

The excess H^+ ions are disposed of by neutralization resulting from decarboxylation, by transport into the vacuole, or by transport via the phloem into the roots and thence into the soil solution. If the excess H^+ ions are not removed physically or chemically (neutralization) from the cytoplasm, they lead to pH decrease in the cytoplasm [25]. Cytoplasmic pH regulation may most generally be achieved by transport of excess H^+ ions out of the cytoplasm. The sink to which these ions are transported is typically the external solution. Excretion into the surrounding aqueous medium is the usual means of pH regulation in aqueous plants. In the case of land plants, some species counteract the change in cytoplasm pH by excreting H^+ ions into the soil solution and at the same time taking in basic nutrient cations to balance the charge (process 9 in Fig. 1). Thus, the soil becomes more acidic [26].

2.1.2.   Uptake and Assimilation of Nitrogen

Plants take up N in three main forms—as an anion (nitrate, NO_3), as a cation (ammonium, NH_4^+), or as a neutral N_2 molecule (N_2 fixation, in legumes only). Depending on the form of N taken up and the mechanism of assimilation in the plant, excess uptake of cations or anions may occur [27–30]. To maintain charge balance during the uptake process, H^+, OH^-, or HCO_3^- ions must pass out of the root into the surrounding soil. The H^+ ions may be derived from the dissociation of organic acids within the cell and OH^- ions from the decarboxylation of organic acid anions. It has been shown that whereas the uptake of NH_4^+ and fixation of N_2 result in a net release of H^+ ions (process 6 in Fig. 1), uptake of NO_3^- can result in a net release of OH^- ions (process 1 in Fig. 1) [31–36].

Nitrogen Fixation.   In the case of N_2 fixation, the neutral N_2 can be assimilated into protein, and no charge imbalance is generated across the soil–root boundary (process 7 in Fig. 1). Many legumes, however, commonly export H^+ ions into their rhizosphere when actively fixing N_2 [27,37–39]. The generation of this acidity is dependent on the chemical nature of compounds that are formed during C and N assimilation (e.g., amino acids). Part of the H^+ ions generated within the legume root comes from the dissociation of the carboxyl groups of amino acids (process 8 in Fig. 1). The acidity generated by fixation of N_2 in
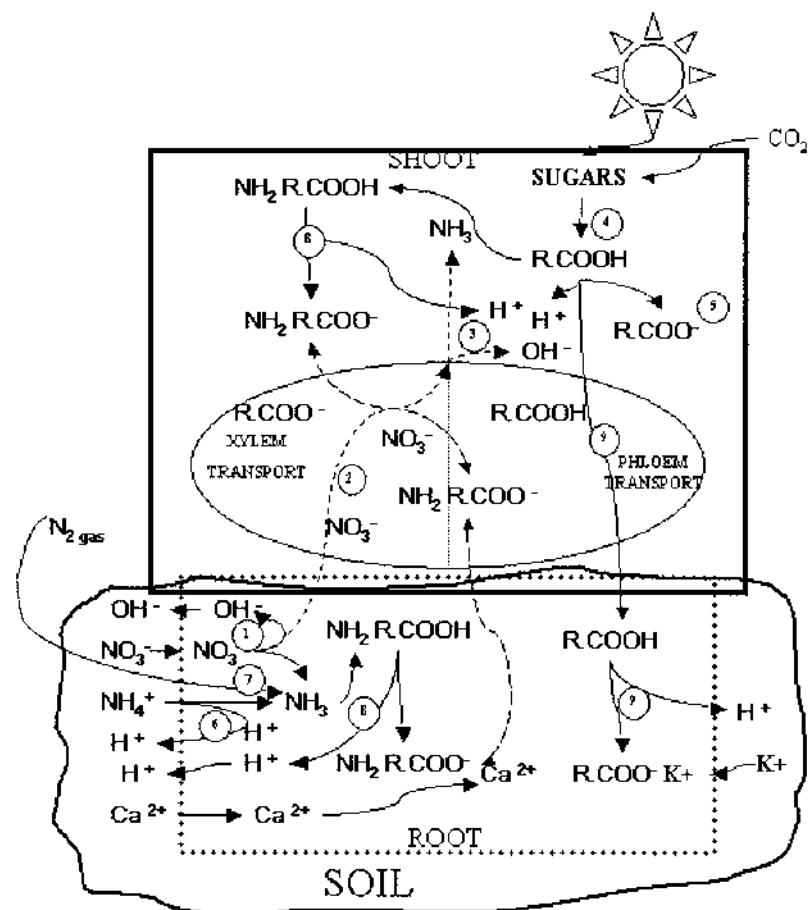
FIGURE 1 Processes of nitrogen and carbon assimilation in plants that influence rhizosphere acidity. The encircled numbers represent (1) nitrate assimilation in roots, (2) xylem transport of nitrate to shoot, (3) nitrate assimilation in shoot, (4) synthesis of organic acid from sugars, (5) dissociation of organic acid (e.g., malic acid) in the shoot, (6) assimilation of ammonium in roots, (7) biological nitrogen fixation, (8) dissociation of amino acid, and (9) dissociation of organic acid (e.g., malic acid) in the root.

legumes has been found to be equivalent to the excess uptake of cations over anions by the plant and to vary from 0.2 to 0.7 mole H^+ per mole of fixed N [37–40]. The reason for the generation of acidity, even when no ionic species of N are taken up by the plant, is that basic cations are imported into the legume in exchange for H^+ ions generated during C assimilation into carboxylic acids. In order to maintain pH balance, these H^+ ions are subsequently exported from the roots, generating acidity in the soil.

Some tropical legumes, however, do not apparently acidify their rhizospheres as much as do temperate legumes when actively fixing N_2 [41]. Part of the reason for this is that their NH_3 assimilation products appear to be ureides (allantoin and allantoic acid) that have high pK_a values (e.g., allantoin pK_a 8.96) and are therefore unlikely to dissociate and donate H^+ ions at cytoplasmic and xylem pH values. Thus, we find that many tropical legumes accumulate less cations than temperate legumes [42].

The amount of H^+ ions released during N_2 fixation is really a function of C assimilation and therefore depends mainly on the form and amount of amino acids and organic acids synthesized within the plant [41]. The rate of acidification by a number of temperate and tropical legumes has been examined in many studies [39,43–45], as measured by uptake of excess cations over anions. Although the excess cation values varied widely between the legume species, removal of plant biomass from the field, rather than concentration of excess cations, was considered to be the major determinant of legume-induced soil acidification.

Ammonium and Nitrate Assimilation.   When ammonium (NH_4^+) assimilation occurs in roots, deprotonation of NH_4^+ (the deprotonation product is represented as amide nitrogen R—NH_2) releases 1 mole of H^+ per mole of NH_4^+ (process 6 in Fig. 1) [Eq. (1)]. Additional small amounts of H^+ ions are generated during the assimilation of R—NH_2 into amino acids and proteins that have isolectric pH values lower than the cytoplasmic pH. For example, Breteler [46] observed that sugar beet plants supplied with ammoniacal nitrogen released 1.1 to 1.2 H^+ ions per NH_4^+ ion taken up. The specific reason for this additional H^+ ion input is that, in most plants, NH_3 is initially assimilated into the dicarboxylic amino acids, aspartate and glutamate [47,48]. Aspartate and glutamate are strong carboxylic acids that dissociate to produce H^+ ions at cytoplasm and xylem pH values. In order to maintain a pH balance, the plant exports the dissociated H^+ ions in exchange for cations from the rooting media. For NH_4^+ assimilation to occur in shoots, NH_4^+ is transported up the xylem with a companion malate ion [24]. The H^+ ions released when NH_4^+ is deprotonated in the shoots can be neutralized by OH^- ions generated during decarboxylation of malate; alternatively, undissociated malic acid may be formed and translocated to the root. Maintenance of cytoplasmic pH by this process is known as the "biochemical" or "malate" pH stat [24,49].

$$NH_4^+ + R\text{—}OH \rightarrow R\text{—}NH_2 + H_2O + H^+ \qquad (1)$$
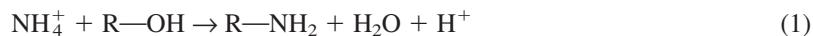
When plants take up nitrogen in the form of NO_3^- ion, the NO_3^- ion is first reduced to ammonia, which is subsequently assimilated into amino acids. When NO_3^- is reduced in roots, 1 mole of OH^- ion is produced for every mole of NO_3^- reduced to NH_3 [50] [Eq. (2)]. When NH_3 is assimilated into amino acids, small amounts of H^+ ions are produced through the dissociation of carboxyl groups of amino acids. The resulting negative charge on the carboxylate group can be balanced by the basic cations that entered the root to balance NO_3^- uptake. The net excess of OH^- ions can either be excreted into the rooting media [33,35,51] or neutralized by the malate pH stat [24,26]. When NO_3^- is reduced in the shoot in order to maintain pH balance in the shoot, the OH^- ions released must be neutralized by the malate pH stat described earlier. Unlike the root, the shoot has no external medium in which to excrete the net OH^- ions produced in the process of NO_3^- assimilation. Malate or another organic anion (e.g., oxalate), along with the cation, is either stored in the vacuole of shoot cells or moves to roots, where decarboxylation of malate in the roots releases CO_2 and OH^- ions, both of which can be excreted into the nutrient medium.

Thus, if NO_3^- is entirely assimilated in roots, the amount of OH^- ions produced is often close to 1 mole per mole NO_3^- taken up. If NO_3^- is assimilated in shoots, however, depending upon the storage capacity of the shoot for products of malate decarboxylation, the amount of OH^- ions released ranges from 0 to 1 mole per mole of NO_3^- taken up.

$$NO_3^- + 8H^+ + 8e^- \rightarrow NH_3 + 2H_2O + OH^- \qquad (2)$$

2.1.3 Uptake and Assimilation of Sulfur

Sulfate (SO_4^{2-}) is assimilated into sulfur-containing amino acids (cysteine, cystine, and methionine) in the form of sulfhydryl (—SH) groups. This reduction process is similar to NO_3^- assimilation and produces 2 net moles of OH^- for each mole of sulfur assimilated [Eq. (3)] [36]. On decomposition of sulfhydryl-containing amino acids, two H^+ ions are generated for each mole of —SH oxidized to sulfate. Because plants require 10 times less S than N (e.g., 4 g S kg^{-1} vs. 40 g N kg^{-1}), assimilation of SO_4^{2-} has only a small effect on proton balance in plants, and likewise decomposition of S-containing proteins contributes little to acid generation in soils.

$$SO_4^{2-} + 8H^+ + 8e^- \rightarrow SH_2 + 2H_2O + 2OH^- \qquad (3)$$

2.2 Soil-Induced Processes

2.2.1 Decomposition of Organic Matter

As microorganisms decompose and respire soil organic matter, they release CO_2 [Eq. (4)]. The concentration of CO_2 in the soil air is normally between 0.15 and 0.65% (v/v) [52], and the pKa for the reaction is around 6.1.

$$\text{Organic carbon (C)} + O_2 \rightarrow CO_2 \qquad (4)$$

CO_2 dissolves in water to form carbonic acid (H_2CO_3). Carbonic acid in the soil dissociates to form H^+ ions [Eq. (5)]:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{5}$$

The continuous production of CO_2 through soil and root respiration drives this reaction to the right. The concentration of CO_2 in the soil air spaces is usually at least 10 times greater than that in the atmosphere, so the strength of soil acid from this source is considerably greater than that from CO_2 dissolved in rainwater. However, acidic soil solutions of pH 5 hold very little CO_2. Thus, respiration is unlikely to cause soil pH to drop below 5.

Soil microorganisms produce organic acids when they are decomposing plant litter rich in organic compounds but low in the concentrations of organates ($RCOO^-$) balanced by basic cations (Eq. 6).

$$\text{Organic C} \rightarrow RCOOH \rightarrow RCOO^- + H^+ \tag{6}$$
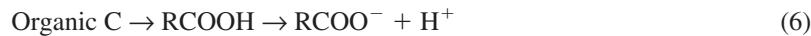
A number of low-molecular-weight organic acids have been isolated from soils [53–55]. Depending upon the nature of the plants growing in a particular soil, different types of plant litter are produced and different amounts of organic acids are generated. The litter layers derived from the great kauri trees in Northland of New Zealand produced large quantities of organic acids; i.e., their litter is not rich in cations. Not only did these litters acidify the soil, but their organic acid decomposition products caused many minerals and plant nutrients to be mobilized and leached from the acidified layer. In general, forest soils that have thick litter layers tend to be more acidic than grassland soils. Further, the litter from conifers tends to produce more organic acids when decomposed than the leaf fall from deciduous woodlands [56].

2.2.2   Transformation of Nitrogen

Ammonification.   Ammonification describes enzymatically catalyzed microbial processes that hydrolyze organic N compounds to yield NH_4^+ ions. The process includes enzymatic deaminization of amino compounds derived from proteins, amino-polysaccharides, and nucleic acids and enzymatic hydrolysis of urea added through fertilizer application and urine deposition. These two reactions can be expressed as follows [Eqs. (7) and (8)]:

$$\underset{\overset{|}{NH_2}}{R\text{—}CH\text{—}COOH} + H_2O + 2H^+ + 2e^- \xrightarrow{\text{enzymatic deamination}} \tag{7}$$

$$R\text{—}CH_2\text{—}COOH + NH_4^+ + OH^-$$

$$NH_2\text{—}CO\text{—}NH_2 + 3\,H_2O \xrightarrow{\text{hydrolysis}} 2NH_4^+ + 2OH^- + CO_2 \tag{8}$$
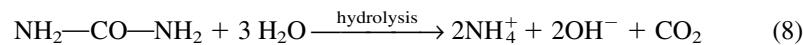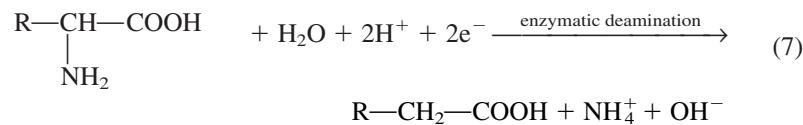
The ammonification process results in the consumption of H^+ ions (or release of OH^- ions). This is the main reason why soon after urea application or urine deposition, the pH around the urea granule and the urine spot increases to al

kaline conditions (around pH 7.5 to 8.0). The alkaline pH conditions induce the conversion of NH_4^+ ions to NH_3 gas, leading to the volatilization loss of ammonia. However, subsequent conversion of NH_4^+ ions to NO_3^- ions results in the release of H^+ ions, leading to soil acidification (see later).

Nitrification.   The process whereby NH_4^+ is oxidized to yield NO_3^- ions is referred to as nitrification. Simplistically, the process can be considered in two steps: oxidation of NH_4^+ to NO_2^- and subsequent oxidation of NO_2^- to NO_2^-. The overall reaction can be expressed as follows [Eq. (9)]:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad (9)$$
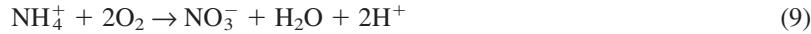
Both heterotrophic and autotrophic microorganisms are involved in the oxidation of NH_4^+ to NO_3^-. Groups of autotrophic bacteria, *Nitrosomonas* and *Nitrobacter,* have been considered the most important nitrifying microorganisms in many agricultural soils, but the importance of their role in pasture soils is not clear.

Whereas the ammonification process results in the release of OH^- ions, the nitrification results in the release of H^+ ions. Combined ammonification [Eq. (8)] and nitrification [Eq. (9)] of organic N compounds, including urea, in theory generate one net mole of H^+ for every mole of N transformed. Oxidation of ammoniacal fertilizers can generate two net moles of H^+ for every mole of N. This is consistent with the observation made by many workers that the extent of soil acidification was generally higher with ammoniacal than with urea fertilizers. Addition of basic nitrate fertilizers such as $Ca(NO_3)_2$ and $NaNO_3$, however, causes little change or sometimes increases the soil pH [14,15,22,23,57–60].

Denitrification.   Denitrification is defined as the microbial reduction of NO_3^- to gaseous N either as molecular N_2 or as an oxide of N under anaerobic conditions. The reactions involved can be simplified as follows [Eq. (10)]:

$$2NO_3^- + 2H^+ \rightarrow N_2 + 2.5\,O_2 + H_2O \qquad (10)$$

Denitrification can also occur from incomplete nitrification in the presence of high NH_4^+ concentrations and low oxygen supply [Eq. (11)].

$$2NH_4^+ + 2O_2 \rightarrow 2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4H_2O \qquad (11)$$
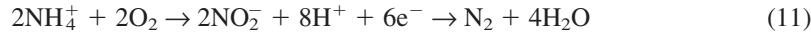
The denitrification reactions that consume H^+ ions are essentially the reverse of those for nitrification in which H^+ ions are produced [Eq. (9)]. Thus, the amount of acidity entering and remaining in the soil from ammoniacal N sources depends largely on the relative magnitudes of the nitrification and denitrification processes [61]. One mole of H^+ ions is consumed per mole of NO_3^- or NO_2^- reduced to N_2. The combined sequence of organic N decomposition involving ammonification and nitrification followed by denitrification creates no net proton gain.

Ammonia Volatilization. Ammonium ions in an alkaline medium dissociate into gaseous ammonia, which is subject to volatilization loss [62] [Eq. (12)]. During NH_3 volatilization, the pH of the soil decreases due to the consumption of OH^- ions (or release of H^+ ions) as NH_4^+ is converted to NH_3. Ammonia volatilization occurs when the soil pH is high (>7.5). In the case of urea nitrogen, the initial increase in soil pH through the ammonification process is likely to result in ammonia volatilization.

$$NH_4^+ + OH^- \rightarrow NH_3 \uparrow + H_2O \qquad (pK_a \ 7.6) \tag{12}$$
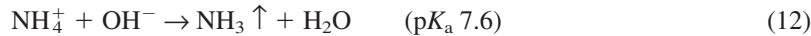
2.2.3 Transformation of Sulfur

In aerobic soils, a large proportion of S is present in organic form in recent litter and roots and more humified organic matter. Sulfur in soil organic matter and plant litter is mainly present as sulfhydryl (—SH) groups in proteins, nucleic acids, and sulfolipids and bonded directly to C. Protons are produced during the mineralization and subsequent oxidation of S in soil organic matter [Eq. (13)].

$$\text{Organic S} + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \tag{13}$$
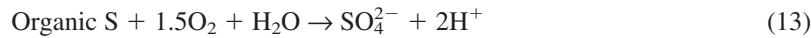
As soil bacteria and fungi grow on plant litter and soil organic matter rich in C and poor in S, soil solution SO_4^{2-} may be immobilized. In this case, Eq. (13) is reversed and becomes a proton-consuming reaction as SO_4^{2-} is assimilated to microbial protein.

In periodic anaerobic conditions that occur following aerobic generation of SO_4^{2-}, the oxygen concentration may be depleted by rapidly growing bacteria. Some bacteria have the capacity to use SO_4^{2-} as a terminal electron acceptor for fermentation. The result is proton consumption as SO_4^{2-} is reduced along a chain of intermediate compounds to H_2S. It is common for H_2S to react with metal ions to precipitate as metal sulfides. This process is a proton-consuming process. However, when these metal sulfides are reoxidized, they generate protons and acidify the soil. This sequence of reactions is common in soils used for lowland rice cultivation and results in a phytophilic neutral pH when waterlogged but can create low phytotoxic pH when the soil is in the aerobic state.

Elemental sulfur (S°) is frequently used as the ultimate high analysis S fertilizer or in a finely divided form as a fungicide. When elemental sulfur is added to soils, it is oxidized to sulfuric acid that dissociates into SO_4^{2-} and H^+ ions [Eq. (14)].

$$2S° + 2H_2O + 3O_2 \rightarrow 2SO_4^{2-} + 4H^+ \tag{14}$$
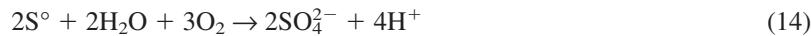
In some soils, a portion of the acidity is neutralized by the OH^- ions released during the ligand-exchange adsorption of SO_4^{2-}. Increases in soil pH due to the ligand-exchange adsorption of SO_4^{2-} have often been observed in soils rich in variable charge components, such as iron and aluminum oxides [20]. This process

is commonly referred to as a "self-liming effect" [63]. The self-liming effect is based on the adsorbed SO_4^{2-} displacing OH^- from hydrous iron and aluminum oxide surfaces, followed by hydrolysis and precipitation of exchangeable aluminum as aluminum hydroxide.

3 NUTRIENT CYCLING PROCESSES THAT LEAVE SOIL ACIDIC

3.1 Uncoupling of Nutrient Cycles

In a closed system, where C, N, and S cycling processes are in steady state and there is no net gain or loss of nutrients, no net generation of H^+ ions occurs by nutrient transformations. For nitrogen, this point has been clearly presented by Helyar [64], Van Breemen et al. [65], and Breeuwsma and De Vries [66]. The net H^+ ions generated by ammonification and nitrification of R—NH_2 to NO_3^- are subsequently neutralized when H^+ ions are consumed during the reduction of NO_3^- and synthesis of R—NH_2 in the plant (processes 1 and 3 in Fig. 1). However, these two H^+ ion-balancing processes are spatially compartmentalized between the soil and the plant and are linked through the plant uptake of highly mobile NO_3^- and the return of organic N to the soil as plant residue or animal excreta. Changes in the amounts of these forms of N and/or their loss from the cycle therefore uncouples the H^+ balance and leads to permanent soil acidification.

   To improve the productivity of soils to economic levels, the plant-available pool of N is increased either by stimulating biological fixation of N_2 in situ or by the application of N fertilizers or manures. As N input increases, it is likely that accumulation of soil organic N, removal of organic N products, and leaching of increasing quantities of NO_3^- occur. Depending upon the form of N inputs into the farming system, each of these changes will induce an increase in soil acidity.

3.2 Accumulation of Soil Organic Matter

The following two scenarios can be presented in which the accumulation of soil, plant, and animal organic N will result in permanent soil acidification:

1. When uptake and assimilation of NH_4^+ or N_2 occur in plants, H^+ ions are excreted into the rhizosphere soil. If soil organic N or litter N in a forest ecosystem accumulates, the OH^- ion generating processes (ammonification and decarboxylation of organic acid anions) are uncoupled from the H^+ ion generating processes in the rhizosphere. As more organic N accumulates in the rhizosphere, acidity should increase, eventually affecting bulk soil pH [5,67–69].
2. When fertilizer NH_4^+ is nitrified, two net H^+ ions are generated per N atom. These H^+ ions can be neutralized only if all the NO_3^- produced is

taken up and assimilated into plant organic N (one OH^- is either extruded into the rhizosphere or stored as organic anion in the plant) and the plant organic N (or breakdown products, e.g., animal excreta) is subsequently ammonified and the organic anion decarboxylated upon decomposition of the plant [70]. Thus, only if all N returns to the input form (NH_4^+) will there be neutrality. If organic N accumulates, the NH_4^+-fertilized system can generate an excess of one H^+ per atom of N accumulated.

Similarly, if instead of accumulating, plant or animal products are removed, nonneutralized H^+ ions remain in the soil. This may also include the uneven transfer of animal excreta within one paddock or loss of excreta to unproductive areas of the farm, such as raceways and yards. Losses of N through NH_3 volatilization or denitrification produce permanent soil acidity only when the N input is added in NH_4^+ form through ammoniacal fertilizer and ammonium-rich wastewaters, such as dairy and piggery effluents.

3.3 Leaching of Nutrients

In most soils, NO_3^- is more readily leached than SO_4^{2-}. Nitrate leaching induces permanent soil acidity only when the loss of NO_3^- uncouples an H^+ ion-balancing system. The following two scenarios can be presented in which the uncoupling of NO_3^- leaching and an H^+ ion-balancing system will lead to permanent acidification:

1. If NH_4^+ or R—NH_2–based fertilizers are added and are subsequently oxidized to NO_3^- in the soil, two (nitrification) and one (ammonification + nitrification) net H^+ ions are generated, respectively. These H^+ ions can be neutralized only if the NO_3^- is completely transformed by the N cycle back into the original input forms. If NO_3^- is lost from the system, the H^+ remains as permanent soil acidity [64].
2. If we consider N transformations only, uptake and assimilation of N_2 into plant protein constitute a proton-neutral process. During the decomposition of the plant protein, through various breakdown products (e.g., urea in animal excreta) to NH_4^+ and then via nitrification to NO_3^-, 1 mole of H^+ ions is generated per mole of N transformed. Unless all the NO_3^- is reassimilated by plants or microorganisms into protein, the excess H^+ ions from the nitrification of R—NH_2 will remain in the soil.

In both of the preceding cases, the surplus H^+ ions will remain in the soil when cations other than the H^+ ions are leached as companion ions with the negatively charged NO_3^- ions [40,61]. It is the mobile exchangeable basic cations, Ca^{2+}, Mg^{2+}, K^+, and Na^+, that are usually leached in exchange for H^+. As soil acidity accumulates, the concentration of basic cations in soil decreases, resulting

in the leaching of H^+ ions as the companion cation. Thus, in very acid soils, NO_3^- leaching may induce less H^+ accumulation than in soils high in exchangeable basic cations. In extreme cases, leaching of H^+ ions with NO_3^- could be a cause of subsoil and ground water acidification (for further discussion see Chapter 3).

3.4 Fertilizer Reactions

As discussed earlier, application of N fertilizers, such as urea and ammonium sulfate, to soils can produce H^+ ions through oxidation of NH_4^+ ions to NO_3^- ions (nitrification). Because the NO_3^- ions are not strongly adsorbed by the soil, it is common that some of the NO_3^- ions not taken up by the crop are liable to leach or move down through the soil. The negatively charged NO_3^- ions are accompanied by positively charged basic cations, such as Ca^{2+}, Mg^{2+}, K^+, and Na^+, in order to maintain the electric charge on the soil particles. It is the exchange of these ions on cation exchange sites for H^+ and the loss of NO_3^- ions that can potentially generate OH^- ions (during plant uptake) and accelerate the acidification process.

The amount of acid produced by N fertilizers depends on the amount of NO_3^- removed by plant uptake and leaching. It is estimated that approximately 1.72 and 5.24 kg of lime are required to overcome the acidity produced by the application of 1 kg of N as urea and ammonium sulfate, respectively. Therefore, if N is added as urea (46% N) at a rate of 25 kg N per ha, then 43 kg lime per ha is needed to neutralize the acidity produced.

In legume-based pastures, phosphate fertilizers produce acids by two processes, namely (1) fertilizer reaction with the soil and (2) in P-deficient soils, stimulation of legume growth and nitrogen fixation. Dissolution of superphosphate fertilizers (mostly monocalcium phosphate) in soils results in the production of dicalcium phosphate and phosphoric acid close to the fertilizer granules [Eq. (15)]. The phosphoric acid dissociates to phosphate and H^+ ions. A fraction of the H^+ ions produced is neutralized by OH^- ions released during the ligand-exchange adsorption of phosphate ions by soil components. It is estimated that at an annual application rate of 400 kg single superphosphate (10% P) per hectare, approximately 32 kg lime is required to neutralize the acid produced directly by fertilizer dissolution.
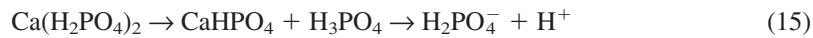
$$Ca(H_2PO_4)_2 \rightarrow CaHPO_4 + H_3PO_4 \rightarrow H_2PO_4^- + H^+ \tag{15}$$

When elemental sulfur is added to soils, it is oxidized to sulfuric acid that dissociates into SO_4^{2-} and H^+ ions [Eq. (14)]. It is estimated that a maximum of approximately 3.1 kg of lime is required to neutralize H^+ produced from the oxidation of 1 kg of elemental sulfur. In both cases of adding P and S^o fertilizers to legume-based pastures, the extra N input and cycling from the fertilizer-responsive legume result in greater soil acidification than that caused directly by fertilizer reactions with soils.

4 A SYSTEM CASE STUDY—ACIDIFICATION IN LEGUME-BASED PASTURES

Virtually all New Zealand's and Australia's animal-based exports are produced through the management of legume-based pastures. On many productive lowland pastures, liming to overcome continuing soil acidification has become a regular management practice required to maintain pasture production and animal health [11] (see Chapter 11).

The current method for estimating lime requirements in pasture soils in New Zealand [71] is based on the relationship between soil pH and response to lime. This method has major limitations mainly because this relationship is rather poor [72] and is derived empirically rather than from knowledge of the underlying mechanisms of soil acidification [12]. The incorporation of a mechanistic model for predicting soil acidification rates into the current lime requirement model is expected to improve the accuracy of this approach. Furthermore, in situations where the optimal soil pH is known, a soil acidification model can be used to calculate the amount of lime required for maintaining the soil pH at the desired level. In addition, in areas where liming is thought to be uneconomic (e.g., hill and high country farming in New Zealand and areas remote from liming sources in Australia) because of high application costs, a predictive soil acidification model is useful in defining pasture sustainability for these areas.

A number of models have been developed to predict soil acidification that incorporate the mechanisms of various processes responsible for soil acidification [1,2,12,72]. These models are discussed in detail elsewhere in this book (see Chapter 11). Briefly, Helyar and Porter [1] presented a framework for estimating the net input of H^+ ions into a system from processes involving the various nutrient cycles that occur in the soil. Sinclair [72] considered NO_3^- leaching and nutrient transfer as the two main causes of soil acidification and presented a model for estimating the animal-induced acidification based on stocking rate. These models require quantitative information on the processes responsible for soil acidification. De Klein et al. [12] extended the model developed by Sinclair [72] to incorporate submodels for estimating the extent of NO_3^- leaching, nutrient transfer or removal, and soil organic matter accumulation.

In this section we illustrate the concept of predicting the rate of acidification and future lime requirement of a soil from knowledge of the gains and losses of C, N, and S from the production system. The simplest system to consider and perhaps the most appropriate to New Zealand and Australia grassland is the one in which all N has entered the "improved" pasture as symbiotically fixed N_2 [2].

4.1 Acidification of the Rhizosphere

The mechanisms generating H^+ ions in the legume rhizosphere were discussed in previous sections. The acidity generated by the assimilation of CO_2 and N_2 in

legumes is equivalent to the uptake of excess inorganic cations over anions by the legume. This assumes that N_2 assimilation into protein is a proton-neutral process. Nyatsanga and Pierre [37] have shown it is reasonable to assume that the amount of net excess cations per unit of plant-N is relatively constant for legume crops. Thus, for a standing legume crop, the number of H^+ ions generated in the rhizosphere soil (R_LH; mol H^+ ha^{-1}) can be estimated from the excess cation/nitrogen ratio and the total amount of N accumulated [Eq. (16)].

$$R_LH^+ = N_a\left(\frac{\Sigma C_L - \Sigma A_L}{N_c}\right) \tag{16}$$

where

N_a = total amount of biologically fixed N accumulated in the standing legume (kg N ha^{-1})

ΣC_L = sum of inorganic cations (Ca^{2+} + Mg^{2+} + K^+ + Na^+) in the legume (mol charge kg^{-1} DM)

ΣA_L = sum of inorganic anions (SO_4^{2-} + $H_2PO_4^-$ + Cl^-) in the legume (mol charge kg^{-1} DM)

N_c = concentration of legume N (kg N kg^{-1} DM).

When N enters the sward only through N_2 fixation, even if the sward contains grasses that take up NO_3^- or NH_4^+ derived from the decomposition of the clover, it can be shown that rhizosphere acidity can be calculated from the excess cationic charge in a mixed sward sample and the accumulated amount of organic N. All N transfers from N_2 to R—NH_2 in the grass have charge balance and cause no net change in pH. Net rhizosphere H^+ arises solely from the synthesis and dissociation of organic acids within the plant. For mixed clover–ryegrass swards at seven sites in the lower North Island of New Zealand, the excess cation/nitrogen ratio in the clover plant approximating 0.4:1, was found to be very similar to that in ryegrass [73]. This ratio is similar to that obtained for alfalfa (0.41:1) [37] and for soybean (0.36:1) [41].

4.2 Acidification Due to Organic Matter Accumulation and Product Removal

The H^+ ions exported from mixed sward roots in exchange for the accumulation of anionic charge will remain in the rhizosphere soil if the organic anions synthesized by the plant and their associated basic cations either accumulate in organic matter within the pasture system or are removed from the site of N_2 and CO_2 assimilation. Such removal occurs with the removal of animal products and excreta from a legume-based grazing system. In such a system the acidity generated in the rhizosphere soil of the sward could be estimated from Eq. (17).

Permanent acidity in the sward (R_sH^+) in mol H^+ ha^{-1} is given by

$$R_sH^+ = (\Delta SN + XN)\left(\frac{\Sigma C_s - \Sigma A_s}{N_c}\right) \tag{17}$$

where ΔSN is the increase in soil, plant, or animal N (kg ha^{-1}), XN is the amount of N exported in animal products and excreta (kg ha^{-1}), and ΣC_s, ΣA_s, and N_c for the sward are as defined in Eq. (16) but for practical purposes could be measured as the mean annual sums of accumulated cations and anions and N concentration of the sward. This approximation assumes that the ratio of excess moles of anionic charge to moles of N in the accumulated organic matter and the organic products that were removed is similar to that in the mixed sward. A more accurate method would be to measure the excess of inorganic cations over anions in the materials removed [1].

4.3   Acidification Through Nutrient Leaching

For every NO_3^- ion leached in the drainage water, one H^+ ion remains at the site of nitrification. This occurs when the cation accompanying the NO_3^- is a basic cation (i.e., other than H^+ ion). Thus, in a system where all N input is derived from biological fixation of N_2, the H^+ ions generated by NO_3^- leaching (L_NH^+) can be calculated from Eq. (18). This assumes that no significant amount of H^+ appears in the drainage water.

$$L_NH^+ = \Sigma NO_{3L}^- \tag{18}$$

where ΣNO_{3L}^- is the cumulative amount of NO_3^- leached (mol charge ha^{-1}).

In most soil acidification models [1,74], NO_3^- leaching is calculated from the difference between the total acid production, as assessed from changes in pH and the pH buffering capacity, and the acid addition from processes other than NO_3^- leaching. De Klein et al. [12] developed a mechanistic model to predict soil acidification for pasture system in which they incorporated a submodel to estimate NO_3^- leaching.

4.4   Predicting Acidification

For working examples of farms mostly dependent upon biological N_2 fixation, we take the examples of the farms given in Table 3 [75]. As no detailed data on drainage water composition are available, Eq. (18) is used to estimate the permanent acidity generated from NO_3^- leaching. Combining Eqs. (17) and (18) gives

$$R_SH^+ + L_NH^+ = \left[(\Delta SN + XN)\frac{(\Sigma C_s - \Sigma A_s)}{N_c}\right] + \Sigma NO_{3L}^- \tag{19}$$

TABLE 3 Nitrogen Balance for the Case Study Farms

Attribute	New Zealand		Australia
	Waikato	Canterbury	
Soil	Yellow brown loam	Yellow brown earth	Xanthozem
Climate	Temperate	Temperate	Tropical
Rainfall (mm)	1600	771	860
Stock	Dairy cattle	Sheep	Beef cattle
Stocking rate (SU ha^{-1})	24	20	5
Pasture	Ryegrass–white clover	Ryegrass–white clover	Verano stylosanthes
Pasture yield (t DM ha^{-1} year^{-1})	16.5	11.0	6.0
N input (kg N ha^{-1} year^{-1})			
Fixation	281	180	43
Rain	3	10	4
Losses (kg N ha^{-1} year^{-1})			
Leaching	110	100	—
Volatilization	24	30	10
Denitrification	30	10	—
Retention in livestock	8	20	4
Livestock products	66	—	—
Animal transfer	46	30	—
Soil gain	—	—	33

Source: Adapted from Ref. 2.

The increases in soil, plant, and animal N (ΔSN), the amount of N exported from the system (XN), and the amount of N leached (ΣNO_{3L}) are given in Table 3. The amount of excess cationic charge per mole of N taken up by plants (($\Sigma C_s - \Sigma A_s)/N_c$) was derived from the data of Metson and Saunders [73]. The amount of H$^+$ ions generated from excess cation uptake ($R_S H^+$) and from NO_3^- leaching ($L_N H^+$) and the amounts of lime ($CaCO_3$) required to neutralize this excess acidity were calculated (Table 4).

Table 4 shows that the net amount of H$^+$ ions generated in the first two farms in New Zealand is much higher than that in the third farm in Australia. This is due to the higher amounts of N cycled, accumulated, and leached in the former farms than in the latter. A number of studies have shown that higher levels H$^+$ ions are produced in New Zealand than in Australia (Table 1).

In the first two New Zealand farms, the predicted amounts of H$^+$ ions generated were higher than those inferred from the annual lime requirement [11] (Table 4). Such an overestimate, based on comparing predicted soil H$^+$ ion gen-

eration with changes in surface soil pH, might be accounted for by macropore flow of urine that bypassed the surface soil. Nitrification of some urea would take place at depth and would result in one net H^+ ion per atom of N remaining in the subsoil. Nitrate would still appear in the drainage water, but as urea had bypassed the topsoil, topsoil pH would remain unchanged. Williams et al. [76] estimated that for a Yellow brown loam soil similar to the one at Waikato, approximately 15% of all urine N could be lost from the topsoil by macropore flow of urine. On the Waikato farm [77] this would amount to 44 kg N ha^{-1} year^{-1}, which is 37% of the entire N appearing in the drainage. If this is taken into account, the net amount of H^+ ion produced would be 7.7 kmol H^+ ha^{-1} year^{-1}, equivalent to a lime requirement of 385 kg year^{-1}, which is very close to the rate recommended by Pringle et al. [11].

The estimated amount of H^+ ions generated in the third farm in Australia (1.08 kmol H^+ ha^{-1} year^{-1}) may be compared with an increase of approximately 1.1 and 0.8 kmol H^+ ha^{-1} year^{-1} in exchange acidity of Coolup sandy soils [78] and the Yellow podzolic soils [5] under subterranean clover pastures in Western Australia and New South Wales, respectively. There is, however, a huge variation in the rate of acidification as shown in Table 1. The extent of soil acidification, as measured by a decrease in soil pH, depends mainly on the pH buffering capacity of the soil. Various soil constituents such as organic matter, Fe and Al oxides, and $CaCO_3$ (in calcareous soil) contribute to pH buffering of soils at different pH values [79–81]. In many Yellow brown loams and Yellow gray earth soils in New Zealand and Xanthozems and podzolic soils in Australia, the rates of soil acidification calculated in the preceding examples may remain unnoticed for several years because these soils can have short-term pH buffering capacities of approximately 90 and 30 kmol ha^{-1} for a unit change in pH, respectively [82]. Thus, in the case of the first two farms where the annual net H^+ ion input into the surface soil is on the order of 1 kmol ha^{-1} it may take 30 years to cause a unit drop in soil pH. It has been observed that continuous pasture of subterranean clover in Aus-

TABLE 4 The Amount of Protons Generated in the Case Study Farms[a]

Farm	Fixed N	ΔSN	XN	Σ NO$_{3L}$	RsH	L$_N$H$^+$	Total H$^+$	CaCO$_3$ requirements (kg ha^{-1} year^{-1}) Predicted	Measured
	(kg ha^{-1} year^{-1})				(kmol H$^+$ ha^{-1} year^{-1})				
Waikato	267 (94)[b]	8	112	110	3.51	7.85	11.36	550	420
Canterbury	180 (20)	20	30	100	1.46	7.14	8.60	430	420
Townsvile	43 (91)	37	0	—	1.08	—	1.80	54	—

[a] Value of $(\Sigma C_s - \Sigma A_s)/Nc$ is taken as 0.41.
[b] Values within parentheses in column two represent the percentage contribution of fixed N to the toal N in the system, the rest coming from rainfall.

tralia has resulted in a decrease in soil pH at a rate of 0.018 to 0.036 pH unit per year, indicating that it takes approximately 27 to 53 years to cause a change of one pH unit [5,6,78,83]. Furthermore, in the longer term these soils are expected to have even greater pH buffering in regions close to pH 5.

5 MINIMIZING SOIL ACIDIFICATION

Acidification of soils under managed ecosystems occurs mainly through uncoupling of the processes generating H^+ and OH^- in the C, N, and S cycles. To minimize the rate of acidification and the negative impacts on agricultural production, three approaches can be taken: (1) reduce the amount of H^+ ions generated, (2) reduce the uncoupling of processes generating H^+ and OH^- ions, and (3) neutralize the acid produced. The rate of acid generation can be altered by selecting the nutrient forms added to soil–plant systems that produce less acid and selecting plant species that do not accumulate cation excesses. Permanent soil acidification can be minimized mainly by reducing the loss of C, N, and S from the system to drainage, product losses, or noncycling pools (e.g., soil organic matter accumulation).

Liming is most commonly practiced to overcome the impact of soil acidification. However, an integrated approach involving liming, management practices, and plant tolerance will probably be necessary, particularly where the acidification potential is high and acidification is likely to extend into the subsoil. Cregan et al. [84] and Helyar [85] identified a number of management practices to minimize soil acidification. These include using less acidifying fertilizers, improving nutrient use efficiency, reducing nutrient leaching losses, and reducing product removal.

5.1 Use of Less Acidifying Fertilizers

Fertilizers vary in their rates of soil acidification. The acidifying effect of fertilizer materials is expressed as acidity equivalent. The *acidity equivalent* is defined as the number of parts of pure lime (calcium carbonate) required to neutralize the acidity caused by 100 parts of a fertilizer material (Table 5). The acidity equivalents reported are only approximate "rule of thumb" values, and the amount of acidity generated is dependent upon the fate of the fertilizer N, P, or S in the system. The number of years required to reduce the pH by one unit by these fertilizers for two soils that vary in their pH buffering capacities are also presented (Table 5). The data indicate that ammonium-based fertilizers produce greater amounts of acidity than the urea- and nitrate-based fertilizers. Nitrate, sulfate, and phosphate rock fertilizers have negative acidity equivalents, indicating that these fertilizers provide some liming value. A number of workers have compared the acidifying effects of various fertilizers under both laboratory [58,86] and field conditions [15,23,59,60] and observed that ammonium-based fertilizers have the highest

TABLE 5 Acidifying Effects of Various Fertilizers

Fertilizers	Acidity equivalent[a]	Acidity produced (kmol H^+ ha^{-1})[b]	Number of years required to reduce the pH by one unit[c]	
			Tokomaru	Egmont
Ammonium sulfate	110	2.60	8	26
Diammonium phosphate	74	2.06	10	33
Urea	79	0.86	25	78
Calcium nitrate	−50	—	—	—
Single superphosphate	8	0.48	45	140
Triple superphosphate	15	0.50	43	135
North Carolina phosphate rock	−50	—	—	—
Potassium sulfate	−64	—	—	—
Elemental sulfur	310	1.55	14	43

[a] kg calcium carbonate 100 kg^{-1} fertilizer; negative value indicates liming value.
[b] N fertilizers = 25 kg N ha^{-1} $year^{-1}$; P fertilizer = 30 kg P ha^{-1} $year^{-1}$; and elemental sulfur = 30 kg S ha^{-1} $year^{-1}$.
[c] pH buffering capacity (kmol H^+ ha^{-1}) = 21.7 and 67.5 for the Tokomaru and the Egmont soil, respectively.

acidifying effect. Choosing a fertilizer with a low or negative acidity equivalent (Table 5) can help to minimize soil acidification.

5.2 Improving Nutrient Use Efficiency

The nutrient use efficiency of plants can be improved through the use of slow-release fertilizers, split application of fertilizers, placement in the root zone, and selection of deep-rooted plant species. Wang and Alva [87] observed that slow-release N fertilizers (isobutylidene diurea and polyolefin resin–coated urea) reduced the leaching losses compared with readily soluble N fertilizers and thereby increased the N utilization by plants. Split application of fertilizers has often increased the nutrient utilization by plants [88]. Perennial pasture species can reduce water losses from deep drainage compared with annual species [89], thereby decreasing the leaching losses of mobile nutrients such as nitrate. Ridley et al. [74] observed higher soil pH values under a *Phalaris*-based pasture than under a comparable annual grass and subterranean clover–based pasture; the net acid addition to soil was calculated to be 0.7 kmol H^+ ha^{-1} $year^{-1}$ less under the *Phalaris* pasture. A decrease in NO_3^- leaching under these species is considered to be the main

reason for lower acidification rates, and thus these species have the potential to re-
duce soil acidification.

5.3 Reducing Nutrient Leaching Losses

In the N cycle, the NO_3^- leaching is considered to be the major factor inducing per-
manent soil acidification. It has often been found that cultivation increases the
leaching losses of NO_3^- by enhancing the ammonification–nitrification process.
Meek et al. [21] have shown that NO_3^- leaching is higher under convention tillage
than under direct drilling. Evans et al. [90] have observed greater accumulation of
NO_3^- under a grain legume (pea) than a cereal (barley) crop, indicating greater gen-
eration of H^+ ions. The greater NO_3^- concentrations are likely to accelerate NO_3^-
leaching, leaving soil acid non-neutralized. Nitrate leaching also enhances the
leaching loss of valuable basic nutrient cations. McKenney et al. [91] have shown
that the addition of residues with a high C/N ratio increases the immobilization of
N and thereby decreases the leaching losses. Soil amendment with cereal straw has
often been found to be effective in reducing NO_3^- concentration under grain legume
crops, resulting in reduced acidification through reduced NO_3^- leaching. Similarly,
the inclusion of cover crop to reduce soil NO_3^- concentrations may potentially de-
lay the leaching of NO_3^- mineralized during a period of fallowing.

5.4 Reducing Product Removal

Removal of plant residues carrying organic anions and excess cations is likely to
accelerate soil acidification. Similarly, the accumulation of partially decomposed
organic matter in soils causes soil acidification as observed under clover pasture
and lupin–cereal rotations in Australia [9,92]. However, short-term incubation ex-
periments have shown that the addition of organic residues with excess cations in-
creases the pH of the soil [93–95]. Accumulation of organic anions is the primary
source of the potential alkalinity that causes an increase in soil pH if decomposed
by soil microorganisms. The change in soil pH with the addition of organic mat-
ter depends on the rate of release or consumption of H^+ by the organic matter
added to the soils. The degree of consumption or release of H^+ by organic matter
is dependent on its initial content of anion charge balanced by basic cations rela-
tive to undissociated acid groups, the initial soil pH, the dissociation constant
(pK_a) of the remaining undissociated organic acids, the extent of dissociation of
the organic acids when they are released into soil, and finally the extent of de-
composition of the organic matter in the soil.

If the soil pH is less than the pK_a value of the organic acid in the organic
matter, there will be an increase in soil pH due to the association of H^+ ions from
the soil with some of the organic anions [92]. Subsequent decomposition of highly
reduced organic matter is likely to generate carboxylic acids as oxidation prod-
ucts. This is common during the decomposition of C-rich cereal straw, and some

of these carboxylic acids may dissociate. If organic anions are decomposed (respired or decarboxylated), they generate HCO_3^- or OH^- ions.

6 CONCLUSIONS

The incomplete cycling of C, N, and to a lesser extent S in soils under agricultural management has been identified as a major cause of increasing soil acidity. In particular, accumulation of undecomposed soil organic matter rich in organates, losses of organates in products, and inputs of symbiotically fixed N and ammonium-based fertilizers with consequent nitrate leaching are involved in the accelerated acidification of agricultural soils.

It is possible to determine the lime requirement of agricultural soils knowledge of the form of N and S inputs and the quantity of basic cations removed by plants, accumulated in organic products, or lost as companion ions with leached nitrate. For legume-based systems, a useful approximation of this lime requirement can be calculated from the amount of N lost or accumulated in organic products, the excess cation charge in the crop or sward, and an estimate of the quantity of nitrate leached. Combined with a knowledge of soil pH buffer capacities, such calculations are useful to predict the long-term lime requirements of a farming system. Accurate estimates of the rate of soil organic matter accumulation and the quantities of NO_3^- leached are the main knowledge gaps limiting the accuracy of this approach for predicting short-term lime requirements.

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3

Role of Plant Cation/Anion Uptake Ratio in Soil Acidification

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1 INTRODUCTION

Soil acidification is a slow natural process that occurs during pedogenesis and can be either accelerated or slowed down by farming practices. The causes of soil acidification in agricultural systems have been attributed mainly to an imbalance in the carbon and nitrogen cycles [1,2] (see Chapter 2). The major processes leading to soil acidification include (1) net H^+ excretion by plant roots due to excess uptake of cations over anions; (2) removal of alkalinity in farm products such as grain, hay, meat, and wool; (3) accumulation of organic anions in the form of soil organic matter; (4) mineralization of organic matter, nitrification of ammonium, and subsequent leaching of nitrate, and (5) input of acidifying substances such as NH_4^+-based fertilizers.

Topsoil acidity can be effectively ameliorated by liming (see Chapter 11). However, the development of subsoil acidity [3–8] is of particular concern due to the greater cost and difficulty of amelioration.

Plants take up cations and anions from soil solutions to satisfy their requirement for growth. The relative amounts of various ions absorbed from soil solutions by plant roots are determined by the specific plant requirements for these ions and the composition of the soil solution. In most cases, plants take up more

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cations than anions, with a net extrusion of H^+ to maintain the charge balance. This chapter contains a review of available literature on the role of the plant cation/anion uptake ratio in soil acidification, particularly its contribution to the development of subsoil acidification.

2   CATION/ANION BALANCE AND SOIL ACIDIFICATION

2.1   Proton Extrusion and Cation/Anion Balance

There should be no net charge carried across the plasma membrane, except a small charge imbalance caused by the action of the electrogenic H^+-adenosine triphosphatase (ATPase) pumps. Therefore, the uptake of a cation must be accompanied by uptake of an anion(s) of equal but opposite charge or by the extrusion of H^+ or other cations. The reverse is true for the uptake of an anion. Plants generally extrude net excess H^+ when cation uptake exceeds anion uptake and, conversely, extrude net excess of OH^-/HCO_3^- or consume H^+ when anion uptake exceeds cation uptake. These phenomena can be experimentally demonstrated by pH changes in nutrient solution [9] as well as in the rhizosphere of the soil-grown plants by monitoring color changes of pH indicators in the agar overlaid on roots [10] or by using pH microelectrodes [11].

The amount of net excess of H^+ or OH^- excreted by the root is equivalent to the respective excess cation or anion uptake by the plant [12]. A number of studies [e.g., 9,13–15] have shown close relationships between excess ion uptake and release of H^+ or OH^-. For example, when nitrate was the only source of nitrogen, pea plants took up more anions than cations by 1.47 mmol($-$) plant^{-1} at day 21 and by 4.2 at day 42, leading to net OH^- extrusion of 1.41 and 4.44 mmol plant^{-1}, respectively. In contrast, when relying on N_2 fixation, the plants took up more cations than anions by 0.28 mmol($+$) plant^{-1} at day 21 and by 1.51 at day 42 and simultaneously released 0.33 and 1.58 mmol H^+ per plant, respectively [9]. Similarly, when 12 N_2-fixing pasture legumes were grown from 40 to 61 days in nutrient solutions, the amounts of net excess H^+ extruded by the plant roots correlated well with excess cation uptake ($r^2 = 0.94$) with an H^+/excess cations ratio of 1.06 [14].

Unbalanced uptake rates of cations and anions tend to cause cytoplasmic pH changes as well as charge imbalance in the plant. Excess cation uptake by the root is associated with a pH increase in the cytoplasm of the root cells, whereas excess anion uptake is associated with a decrease in cytosolic pH [16]. Plant cells are able to maintain their cytosolic pH and charge balance within relatively narrow limits through (1) proton exchange across the plasma membrane and tonoplast and (2) the formation and breakdown of carboxylic groups that are involved in the consumption and production of protons [17].

2.2 Measurement of Cation/Anion Balance

There are three methods of measuring cation/anion uptake ratios: (1) measuring depletion of ions in the root medium, (2) determining excess cations in tissues, and (3) measuring ash alkalinity after incinerating plant tissues. The nutrients whose content is used in calculating the cation/anion balance in plant tissues are NH_4^+, K^+, Ca^{2+}, Mg^{2+}, and Na^+ (cations) and NO_3^-, $H_2PO_4^-$, SO_4^{2-}, and Cl^- (anions). Other nutrients are present in plant tissues in small amounts and therefore are not included in the calculation. Although soil-grown plants contain appreciable amounts of silicon [18], it is taken up as uncharged hydrated silicic acid (due to its high pK) and hence does not contribute to the charge balance.

2.2.1 Depletion of Ions in Nutrient Solution

This approach involves the sampling of nutrient solution over a period of time and determining the concentration of ions. The amounts of cations and anions taken up by the plant can be calculated from the change of ion concentration in nutrient solution over time. Using this approach in a split-root study, Loss et al. [19] demonstrated that net excess protons were excreted by the roots of *Lupinus angustifolius* (narrow-leafed lupin) where excess cation uptake occurred, and the net excess hydroxyl ions were excreted where more anions than cations were taken up. The amount of net excess H^+ or OH^- extruded was close to the charge difference between amounts of cations and anions depleted from the nutrient solution.

The nutrient depletion method is relatively simple and sensitive for macronutrient cations and anions. The measurable depletion of nutrients can be detected within hours and much earlier in some cases (e.g., K^+ and nitrate), and pH change (i.e., net excess H^+ extrusion) can be measured simultaneously. However, this method may be applicable only to solution culture and is not feasible for long-term studies.

2.2.2 Accumulation of Excess Cations in Plant Tissues

In this method, individual nutrients in plant tissue need to be analyzed. The concentration of excess cations (or excess base, EB) is calculated as the charge difference between non-N cations and non-N anions and expressed as $cmol(+) \, kg^{-1}$ dry weight of plant tissue. Thus

$$\text{Excess cations} = (K^+ + Ca_{0.5}^+ + Mg_{0.5}^+ + Na^+) - (H_2PO_4^- + SO_{4(0.5)}^- + Cl^-)$$

Because excess cations in plant cells are balanced by organic anions, the measurement of excess cations also provides an estimate of the organic anion concentration in the plant. To estimate cation/anion uptake ratios, the uptake of NH_4^+ and NO_3^- needs to be included.

Plant species differ substantially in concentration of excess cations in their tissues, ranging from 25 to 255 $cmol(+) \, kg^{-1}$ in shoots (Table 1). The concentra-

TABLE 1 Acid Production and Shoot Excess Cations or Ash Alkalinity (Excess Bases, EB) of N_2-Fixing Legume Species and Selected Cereal Crops

Species	Acid production (cmol kg^{-1} shoot)	EB (cmol kg^{-1})	Growth conditions	References
Grain legumes				
Cicer arietinum	58	108	Soil, 42 d	20
(chickpea)	44–115	110–144	Soil, various P, 60–64 d	15
		143	Field, maturity	21
	220	177	Solution, 42–49 d	13
Glycine max	72–117	85–104	Soil, 67–73 d	22
(soybean)		109, 101	Perlite+solution, 65 and 105 d	23
		102–142	Perlite+solution, 41–151 d	24
		106–143	Field survey, flowering stage	25
Lathyrus sativus	33	74	Soil, 42 d	20
(grasspea)	144	122	Solution, 42–49 d	13
Lens culinaris	132		Solution, 42–49 d	13
(lentil)				
Lupinus albus	23–43	46–84	Soil, various P, 60–64 d	15
(white lupin)	38	72	Soil, 42 d	20
	126	121	Solution, 42–49 d	13
Lupinus angustifolius	19–74	64–113	Soil, various P, 60–64 d	15
(narrow-leafed		93, 101	Soil, 105 and 82 d	
lupin)	55	122	Soil, 42 d	20
	58–86	96–142	Soil, various K, 55 d	27
		132	Field, maturity	21
	178	167	Solution, 42–49 d	13
Lupinus pilosus	144	139	Solution, 42–49 d	13
(rough-seeded lupin)				
Lupinus luteus		57	Field, maturity	21
(yellow lupin)	31–57	82–107	Soil, various P, 60–64 d	15
	46	96	Soil, 42 d	20
	145	119	Solution, 42–49 d	13
Pisum sativum	27–31	64–68	Soil, 42 d	20
(field pea)	78–115	110	Solution, 42 d	28
		112	Field	21
	95	116	Solution, 42–49 d	13
	132, 120	112, 115	Solution, 21 and 42 d	9

TABLE 1 *Continued.*

Species	Acid production (cmol kg^{-1} shoot)	EB (cmol kg^{-1})	Growth conditions	References
Vicia faba	34	77	Soil, 42 d	20
(faba bean)	32–68	60–122	Soil, various P, 60–64 d	15
		106	Field, maturity	21
	125	145	Solution, 42–49 d	13
Vicia sativa	149	126	Solution, 42–49 d	13
(common vetch)				
Pasture legumes				
Biserrula		65	Field, maturity	21
pelecinus	44–63	106–134	Soil, 49–77 d	29
(biserrula)	5–21	76–160	Soil, various P, 60–64 d	15
Coronilla varia		73–139	Field survey, flowering stage	25
(crown vetch)				
Lespedeza stipulacea (Korean lespedeza)		100–101	Field survey, flowering stage	25
Lotus corniculatus		72–110	Field survey, flowering stage	25
Melilotus spp. (sweet clover)		61–108	Field survey, flowering stage	25
	96–184	118–173	Solution, 28–84 d	30
Medicago murex	47–92	64–131	Soil, 49–77 d	29
(medic)	209[a]	185	Solution, during d 40–61	14
Medicago polymorpha	24–64	76–180	Soil, various P, 60–64 d	15
(medic)	188[a]	164	Solution, during day 40–61	14
Medicago sativa (lucerne)	147–143	101–127	Soil, 131–167 d (2–3 cuttings)	22
		107–130	Field survey	31
	120, 160	145, 105	Solution, 44 and 75 d	32
	141–187	141–169	Solution, 28–84 d	30
		105–173	Field survey, flowering stage	25
Medicago truncatula (medic)	186[a]	156	Solution, during day 40–61	14

(continues)

TABLE 1 *Continued.*

Species	Acid production (cmol kg^{-1} shoot)	EB (cmol kg^{-1})	Growth conditions	References
Ornithopus compressus (yellow serradella)	143[a]	163	Solution, during day 40–61	14
Ornithopus sativus (pink serradella)	78–128	86–158	Soil, 49–77 d	29
		93	Field, maturity	21
	34–58	93–163	Soil, various P, 60–64 d	15
	186[a]	204	Solution, during day 40–61	14
Stylosanthes spp. (stylos)		82–123	Field	7
Trifolium hybridum (alsike clover)		112–148	Field survey, flowering stage	25
Trifolium pratense (red clover)	128–144	129–137	Solution, 28–84 d	30
		106–152	Field survey, flowering stage	25
	180, 150	180, 105	Solution, 44 and 75 d	32
	230	110–180	Soil, 425 d	33
Trifolium repens (white clover)		149–155	Soil, 75 d	34
	120, 190	185, 165	Solution, 44 and 75 d	32
Trifolium vesiculosum	180[a]	177	Solution, during day 40–61	14
Trifolium balansae	190[a]	182	Solution, during day 40–61	14
Trifolium glomeratum	211[a]	235	Solution, during day 40–61	14
Trifolium tomentosum	55–116	85–124	Soil, 49–77 d	29
	265[a]	255	Solution, during day 40–61	14
Trifolium subterraneum (subterranean clover)		45	Soil, maturity	21
		75, 93	Soil, 82 and 105 d	26
		76, 97	Field survey	31
	52–68	88–122	Soil, various K, 55 d	27
	28–57	92–140	Soil, various P, 60–64 d	15
		91–146	Soil, 61–65 d	34, 35
	83–100	100–175	Soil, 49–77 d	29
	188–214[a]	178–193	Solution, during day 40–61	14

(continues)

TABLE 1 *Continued.*

Species	Acid production (cmol kg^{-1} shoot)	EB (cmol kg^{-1})	Growth conditions	References
Vicia villosa (crown vetch)	136–223	130–182	Solution, 28–84 d	30
Cereal crops				
Avena sativa (oats)		48–76	Field survey, flowering stage	25
Hordeum vulgare (barley)		26–49	Field survey, flowering stage	25
Sorghum bicolor (sorghum)		29–44	Field survey, flowering stage	25
Triticum aestivum (wheat)		25	Soil, 82 d, NH_4-N	26
		26	Field, maturity	21
		25–37	Field survey, flowering stage	25
		50–51	Soil, 61 d, NH_4-N	34
		71–73	Soil, 61 d, NO_3-N	34
Zea mays (corn)		38–75	Field survey, flowering stage	25

[a] Acid production was calculated on a dry-weight basis of the whole plants (shoot plus roots).

tion of excess cations is also influenced by plant age, the part of the plant under consideration, and edaphic and climatic conditions [25].

2.2.3 Ash Alkalinity

As opposed to determining excess cations, a simpler alternative method of measuring cation/anion balance in the plants is to measure the ash alkalinity in these tissues. The measurement of ash alkalinity involves the ignition of ground plant materials at 400 to 500°C and the titration of the produced ash with acid to determine the alkalinity caused by excess base cations present in the ash. In the ashing process, organic materials are combusted to volatile gases and the nonvolatile ions remain as alkaline carbonates with small amounts of phosphates and sulfates. However, with ashing at high temperatures, volatile sulfur and chlorine compounds may be lost during combustion [36] and thus may cause relatively higher ash alkalinity.

The ash alkalinity (AA) measured in this way is equal to the sum of the cations absorbed $[\Sigma C^+]$ minus the sum of the anions absorbed $[\Sigma A^-]$ plus the amount of NO_3^- and SO_4^{2-} reduced and minus the amount of NH_4^+ metabolized into uncharged forms [35], that is;

$$AA = [\Sigma C^+] + [NH_{4\,absorbed}^+] - [\Sigma A^-] - [NO_{3\,absorbed}^-] \\ + [NO_{3\,reduced}^-] + [SO_{4\,reduced}^{2-}] - [NH_{4\,metabolized}^+]$$

If both NH_4^+ and NO_3^- are completely converted to NH_3 and SO_4^{2-} reduction is negligible, ash alkalinity is equal to excess cations. Indeed, there is a nearly 1:1 relationship between ash alkalinity and excess cations [e.g., 14,37]. However, the relationship between ash alkalinity and excess cations can also differ for different plant species, which may relate to species differences in nitrogen and sulfur metabolism. For example, in a pot experiment, Tang et al. [20] reported close relationships between ash alkalinity and excess cations in eight legumes. However, ash alkalinity overestimated excess cations in *Lupinus* species, whereas the reverse was true for other temperate legumes.

2.3 Cation/Anion Balance and Soil Acidification

Plants can alter the rhizosphere pH and subsequently the pH of the bulk soil. The generation of rhizosphere acidity or alkalinity is directly related to the processes of ion uptake by plant roots. Rhizosphere acidification can occur when plants take up more cations than anions. Theoretically, if all the plant residues were returned in situ to the soil and no N losses or acid inputs occurred, net acidification of the soil would be zero because of the deacidifying processes occurring during decomposition of plant materials (see later). However, in most agricultural ecosystems where part of or sometimes even the whole plant is removed in harvest or returned to a different horizon in the soil profile, a portion of acidity created in the soil remains.

A well-nodulated legume often accumulates most of its N through N_2 fixation. The N_2-fixing plants take up more cations than anions because they do not rely on uptake of nitrate to satisfy most of their N requirement. Thus, net efflux of H^+ into the rhizosphere occurs, resulting in a decrease in rhizosphere pH. This has been demonstrated in a number of studies, e.g., with *Trifolium pratense* (red clover) [33], *Trifolium repens* (white clover), *Medicago sativa* (alfalfa), *Glycine max* (soybean) [1], and pasture legumes [29]. Acid production due to excess cation uptake by N_2-fixing legumes may be considerable. Nyatsanga and Pierre [22] have shown that a yield of *M. sativa* of 10 t ha^{-1} produced acidity in the soil equivalent to 600 kg $CaCO_3$ ha^{-1}. The amounts of acid generated by various N_2-fixing legumes grown in the glasshouse varied between 5 and 265 cmol H^+ per kg of dry biomass produced (Table 1).

Acid production by nonleguminous species is largely dependent on the amount and proportions of NH_4^+ and NO_3^- present in the soil or supplied as fertilizers and taken up by the plant. NH_4^+ nutrition decreases the pH, whereas NO_3^- nutrition generally increases the pH of root media [38]. The extent of pH changes is also affected by plant species [20,34].

It should be kept in mind that soil acidity developing under crops in the field also depends on (1) total biomass production, (2) whether all or only part of the crop is removed in the harvest, (3) the extent of nitrate leaching after residue de-

composition and mineralization, and (4) the proportion of N absorbed in ammonium and nitrate forms. The more biomass produced, the more acidity generated by roots of the plants reliant on N_2 fixation or receiving NH_4^+-based fertilizers. The removal of seeds at harvest for cereal and pulse crops or a pasture under animal grazing would contribute to the development of soil acidity to a lesser extent than the removal of shoots. Large acidification is expected where nitrate leaching is severe. High rainfall, lack of plant uptake, and factors favoring nitrification enhance nitrate leaching. Application of NH_4^+-based fertilizers increases and while application of NO_3^- decreases acidification [39] (see later).

If all N in a legume is obtained through N_2 fixation, growing such a species would increase the acidity of the root medium by the amount equivalent to the content of excess cations or ash alkalinity of the plant. When plants are reliant on soil N or fertilizer N, the acidity produced can be calculated according to the following equation [40]:

$$\text{Acid production} = (C - A) + 0.946 N_{org} - 2x - y$$

where all parameters are in mmol per plant, $(C - A)$ represents excess cations, N_{org} is plant organic N, and x and y represent the organic N derived from NO_3^- and N_2 fixation, respectively. By using this equation, the input of acid by a crop growing in the field can be calculated.

3 FACTORS INFLUENCING CATION/ANION UPTAKE RATIO AND ACID PRODUCTION

3.1 Plant Species

Striking differences in acid production and capacity to acidify soils exist between plant species growing under same conditions. Generally, legumes cause more soil acidification than nonleguminous species. For example, when supplied with nitrate, *Fagopyrum esculentum* (buckwheat) and *Cicer arietinum* (chickpea) had lower rhizosphere pH than *Triticum aestivum* (wheat) and *Zea mays* (corn) [10,41]. These differences reflected differences in the cation/anion uptake ratios [42]. In a pot experiment with a brown podzolic soil, growing N_2-fixing plants of *Trifolium pratense* resulted in a pH drop from 7.2 to 4.5 after 14 months of growth, whereas ryegrass supplied with NH_4NO_3 hardly changed the pH during the same period [33]. In the field, the legume phase in the rotation has caused greater soil acidification than the cereal crop phase (Table 2).

More soil acidification under legumes than under other species may be attributed to greater excretion of protons due to greater excess cation uptake during N_2 fixation (which minimizes the need for nitrate uptake) or less ability to take up soil nitrate during growth. In addition, legume residues contain high N, resulting in large amounts of nitrate produced during residue decomposition (e.g., *Lupinus*

angustifolius [45]). The leaching of NO_3^- is often 8- to 10-fold greater under leguminous pastures than under grass pastures [46]. In a field study, van Miegroet and Cole [47] reported that only 10 moles of nitrate per hectare per year was leached from the 40-cm layer under *Pseudotsuga menziesii* (Douglas fir), whereas 3640 moles per hectare per year passed that layer under leguminous *Alnus glutinosa* (red alder) forest. As a consequence, the A horizon was more acidified under *A. glutinosa* than under *P. menziesii* over the 50-year period.

Species differences in the extent of acidification exist among legumes. In glasshouse studies, acid production by N_2-fixing legumes ranged from 5 to 265 cmoles of H^+ per kg biomass produced (Table 1). Among temperate grain legumes, *Cicer arietinum* and *Lupinus angustifolius* have a greater acidifying ability than other species. Among pasture legumes, ranking varies between studies, but *Trifolium tomentosum* (woolly clover), *Trifolium pratense,* and *Trifolium subterraneum* (subterranean clover) generally have greater acidifying ability than *Ornithopus* spp. (serradella) and *Biserrula pelecinus* (biserrula).

In a sandy soil with no fertilizer NO_3^- added, the amounts of H^+ produced

TABLE 2 Reported Rates of Soil Acidification Under Various Cropping Systems Involving Legumes (Acidification Rate: kmol ha^{-1} year^{-1})

Cropping system	Soil type	Acidification rate	References
39-year-old pasture			
Clover	Podzolic soil	2.00	43
Phalaris		1.36	
15-year rotation trial			
Continuous lupin	Sandly loam	5.26	4
Lupin: wheat	podzolics	4.11	
Continuous wheat		3.22	
Fenceline survey			
Lupin + weeds	Sandy soils	0.55	5
Lupin: wheat		0.29–0.37	
Wheat: 2 clover phases		0.17	
Clover + weeds		0.21	
Unimproved pasture		0.16	
25-year rotation trial			
Continuous clover	Duplex soil	0.92	44
2 clover: wheat		0.82	
Clover: wheat		0.41	
Continuous wheat		0.35	
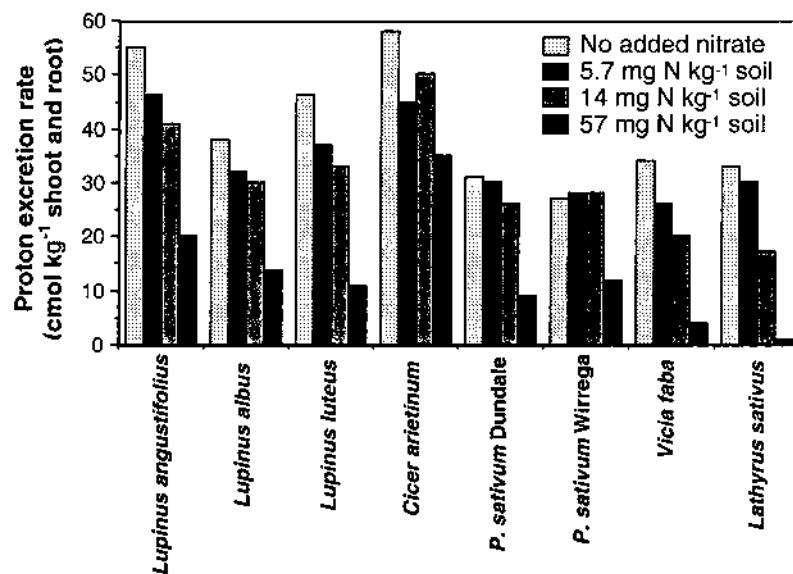
FIGURE 1 Proton excretion rates of eight grain legumes grown at 0, 5.7, 14, and 57 mg N kg^{-1} soil as Ca(NO$_3$)$_2$. (Adapted from Ref. 20.)

per unit biomass varied more than twofold among eight species tested, with *Cicer arietinum* producing the highest and *Pisum sativum* (field pea) the lowest amount of H$^+$ (Fig. 1). Such species variation was even greater when fertilizer NO$_3^-$ was applied.

N$_2$-fixing tropical legumes, with generally lower excess uptake of cations over anions than temperate legumes, have a lower acidifying effect on the rhizosphere and the bulk soil [48]. In addition, the products of N assimilation in tropical legumes appear to be ureides (allantoin and allantoic acid), which have high pK_a values and are therefore unlikely to be dissociated to donate protons at physiological pH values in the cytoplasm and the xylem [49].

In a range of legume species supplied with NO$_3^-$-N as the only N source, the degree of change in the rhizosphere pH depends strongly on the geographic origin of the species [50]. In those originating from acid soils of the humid tropics (e.g., *Glycine max*), no appreciable rhizosphere acidification was found, in contrast to moderate acidification by species from temperate climates (e.g., *Pisum sativum*) and strong acidification by species from semiarid climates [*Cicer arietinum* and *Lens culinaris* (lentil)]. This has important implications for species selection for soils at high risk of acidification.

3.2 Form of Nitrogen

The form of nitrogen supply plays a key role in the cation–anion relationship in plants and hence in net acid production. NH_4^+-fed plants are characterized by a high cation/anion uptake ratio, whereas NO_3^--fed plants have a low cation/anion uptake ratio. By comparison, legumes reliant on N_2 fixation are characterized by a cation/anion ratio greater than 1 (as discussed earlier). For instance, the cation/anion uptake ratios in *Alnus glutinosa* were 3.6–7.0 for plants reliant on NH_4^+, 0.4–0.5 for plants supplied NO_3^- and 2.1–2.2 for N_2-fixing plants during 6 weeks of growth [40].

The acid generated by N_2-fixing legumes was estimated to range from 0.2 to 1.6 moles of H^+ per mole N fixed, whereas the uptake and assimilation of 1 mole of NH_4^+ are associated with the excretion of 1.1 to 1.6 moles of H^+ [51]. In contrast, uptake and assimilation of NO_3^- involve OH^- efflux or H^+ influx. The amount of OH^- produced is close to 1 mole per mole of NO_3^- if NO_3^- is entirely assimilated in roots but ranges from 0 to 1 mole per mole of NO_3^- if NO_3^- is assimilated in shoots [49]. An addition of N as anhydrous ammonia, aqua-ammonia, or urea is not acidifying if the entire amount of added N is utilized by the plant. The increased soil acidification associated with NH_4^+ nutrition and N_2 fixation and increased alkalization associated with NO_3^- nutrition have been demonstrated in glasshouse experiments [e.g., 34] and in field studies [e.g., 8,39]. One should also bear in mind that NH_4^+-N in soil may undergo nitrification, an acid-producing process in itself, with an added problem of subsequent leaching of the nitrate causing topsoil acidification.

The balance between amounts of NH_4^+ and NO_3^- present in soil also greatly influences the relationship between acid production in soil and accumulation of excess cations in the plant. NH_4^+ uptake increases soil acidification (due to NH_4^+/H^+ exchange) but decreases the plant concentration of excess cations or ash alkalinity, whereas the opposite applies to NO_3^- [e.g., 34,35,52]. Increasing supply of NO_3^- decreases soil acidification (due to H^+ being taken up or OH^-/HCO_3^- extruded as NO_3^- is taken up) but increases plant ash alkalinity or the concentration of excess cations. In other words, there is a negative correlation between acid production and excess cations in plants of a given species when supplied with various amounts of NO_3^- [e.g., 20].

The increased excess cations or ash alkalinity present in the plants supplied with NO_3^- has an important implication. When returned to the soil and decomposed, residues containing high ash alkalinity or excess cations have a greater "liming effect" than residues containing low ash alkalinity [21,37]. Thus, a plant species that has a greater ability to use soil NO_3^- not only produces less acidity during the growing season but also neutralizes more acidity when its residues are returned to the soil and decomposed.

3.3 Nutrient Supply

Nutrient deficiencies can change the cation/anion uptake ratio and the pattern of H^+ excretion by the root system. In legumes, deficiency of nutrients such as Ca, P, Co, Cu, and Fe [53], which are directly involved in nodulation and nodule function, may also influence acid production indirectly through affecting N_2 fixation.

The increase in the rhizosphere acidification is a widespread phenomenon of root response to P deficiency in many plant species [54]. For example, when *Brassica napus* (oilseed rape) plants were grown in a P-deficient soil with an initial pH of 6.1, an increase in the rhizosphere pH was associated with excess anion uptake and a decrease of P concentration in the rhizosphere soil solution during the first 2 weeks. Thereafter, a decrease in rhizosphere pH was observed. This decreased rhizosphere pH was associated with excess cation uptake that probably resulted from decreased uptake rates of NO_3^- and increased uptake rates of Ca and Mg [55–57]. Similar responses in terms of rhizosphere acidification and cation/anion uptake ratio have been observed in *Helianthus annuus* (sunflower) under P deficiency [58].

In other instances, P deficiency–induced rhizosphere acidification is related to the extrusion of organic acids. However, the significance of organic acid extrusion in rhizosphere acidification is not clear. The pH decrease of the rhizosphere soil under NO_3^--fed *Lupinus albus* grown in a P-deficient calcareous soil was explained by the excretion of a large amount of citric acid [59]. By contrast, Gardner et al. [60] observed that large quantities of citrate were extruded from cluster (proteoid) roots of P-deficient *L. albus* grown in a mix of sand and vermiculite and that the exudates were neutral in pH because they were citrate anions rather than citric acid. In a sandy soil of pH 5.4, the contribution of organic acids to total acidification appeared to be small under P-deficient *L. albus* and *Cicer arietinum* [15].

Potassium is the most abundant essential cation in higher plants. In charge compensation, K^+ is the dominant cation for counterbalancing organic and inorganic anions in plants [16]. However, application of K_2SO_4 to a K-deficient acidic sand decreased the amount of acidity left in the soil by *Lupinus angustifolius* and *Trifolium subterraneum* per unit biomass produced. Under K deficiency, Ca uptake increased, which led to an increase in excess cation uptake and thus the specific acid production [27].

Dicotyledonous and nongrass monocotyledonous plant species deficient in Fe can induce rhizosphere acidification [61]. However, the effect of Fe deficiency may be of little importance to soil acidification because Fe deficiency generally occurs in high-pH soils. Under Zn deficiency, the rhizosphere acidification by dicotyledonous plants occurs only when the deficiency becomes severe. In *Gossypium hirsutum* (cotton), *Fagopyrum esculentum,* and *Helianthus annuus* grown in nutrient solution with nitrate as the only nitrogen source, the solution pH de-

creased from 6 to 5 under Zn deficiency, whereas the pH increased from 6 to 7 when plants were adequately supplied with Zn. In Zn-deficient plants, excretion of net excess H^+ was associated with a shift in the cation/anion uptake ratio in favor of cation uptake, while nitrate uptake was drastically decreased [62].

3.4   pH

Soil acidity can markedly decrease root growth and nutrient uptake and alter the cation/anion uptake ratio. Low pH generally decreases cation uptake but does not affect or stimulate anion uptake. Hence, low pH decreases excess cation uptake and consequently H^+ excretion. The net H^+ efflux from roots of *Medicago sativa, Trifolium pratense,* and *Trifolium repens* grown for 75 days in the flowing solution culture was not affected by pH between 4.75 and 6.75, but there was an immediate cessation of H^+ excretion when the solution pH was adjusted to 3.75 [32]. Similar effects of low pH have also been found in *Pisum sativum,* with net proton excretion being 2.3 times higher at pH 7 than at pH 4 over the 6-week period [28]. A greater net acidification rate under pasture was recorded for soils with higher initial soil pH [63].

4   CATION/ANION UPTAKE RATIO AND SUBSOIL ACIDIFICATION

Studies in Australia have shown that soil acidification in legume-based agriculture is occurring not only in the topsoil but also in the subsoil to a depth of more than 80 cm [3–6,8,64]. For example, in the central wheatbelt of Western Australia, soil pH increased with increasing depth in the uncleared (native vegetation) sites, whereas with the cleared (farming) sites the lowest pH occurred in the 10- to 20-cm layer; below this layer, the pH increased with depth. Soil pH below the 10-cm depth declined linearly with years of clearing, with an average annual rate of 0.007 unit [6]. Although the cause of subsoil acidification is not yet fully understood, recent studies suggest that acid production by plant roots due to excess cation uptake plays an important role in the development of subsoil acidification [26].

Where in the soil profile acidity generated during plant growth is deposited depends on the distribution of the roots and nutrients, the pattern of nutrient uptake and H^+ extrusion along the roots, and the amount and distribution of plant residues returned to the soil. The pattern of H^+ excretion along the root of *Helianthus annuus, Lupinus angustifolius,* and *Pisum sativum* with a sufficient supply of nutrients was generally uniform [65,66]. By contrast, H^+ extrusion was higher near the root elongation zone than in other root zones in *Zea mays* [67,68]. The H^+ was excreted at the basal portion of *Triticum aestivum* roots supplied with NH_4^+ [69], and OH^- was excreted at the basal portion of the taproot where laterals had initiated [50] or at the root apex [70] of *Z. mays* receiving NO_3^-. In a soil

column experiment in which N_2-fixing *L. angustifolius* and *Trifolium subterraneum* were grown, the decrease in pH down the soil profile was proportional to the root length density [26].

The pattern of H^+ excretion along the root is also influenced by the distribution of nutrients. Using a split-root technique, Römheld [50] demonstrated that *Zea mays* roots supplied with NH_4^+ acidified the rhizosphere, whereas those fed with NO_3^- increased the rhizosphere pH. Loss et al. [19] reported that up to twice as much H^+ was excreted in root zones of nodulated *Lupinus angustifolius* where 1.2 mM K was applied than in zones where K was not supplied. Similarly, Ohwaki et al. [71] showed that the presence of cations in the nutrient solution is required for proton exudation in order for nonspecific H^+/cation antiport to function in roots of *Cicer arietinum.* More recently, C. Allmark et al. (unpublished) showed that greater acidification occurred in the root zone of N_2-fixing *L. angustifolius* where full nutrients (without N) were supplied than in the zone receiving Ca and B only. The amounts of H^+ released in different root zones were related to excess uptake of cations over anions.

Nutrients may be distributed unevenly in soils, both vertically and horizontally. The uneven supply of nutrients along the root axis can markedly affect root distribution and proliferation, which in turn influence the pattern of H^+ extrusion in the soil profile. Root growth is stimulated by localized supply of nutrients or in a nutrient-rich zone [72]. Over a threefold increase in root growth was observed in *Hordeum vulgare* in response to a localized supply of P [73]. In a soil column study in which basal nutrients were applied only to the top 10 cm, 60–70% of the total root length of *Lupinus angustifolius* and over 50% of *Trifolium subterraneum* were distributed in that layer. By comparison, root length density tended to increase with depth when the nutrients were applied uniformly throughout the column [26]. The effect of localized nutrient supply in enhancing root growth has been suggested to be controlled by the apical root meristem and supply of carbon assimilates [74].

Plant species differ greatly in root morphology (diameter, density, etc.) and root distribution in the soil profile and therefore display different patterns of nutrient uptake and H^+ excretion along the root axis as well as down the soil profile. Dicotyledons have a main taproot with fewer laterals, whereas monocotyledons have a fibrous root system [75]. Grain legumes usually have a deeper root system than pasture legumes and acidify deeper soil layers when excess uptake of cations over anions occurs. On deep yellow sands in the Western Australian wheatbelt, the average root diameter of *Lupinus angustifolius* was 0.5 mm, about twice that of *Trifolium subterraneum* or *Triticum aestivum.* Of the total root length, 40% for *L. angustifolius,* 51% for *T. aestivum,* and 70% for *T. subterraneum* occurred in the top 20 cm of soil [76]. Indeed, in a field survey, Loss et al. [5] observed more soil acidification in deeper layers of soil profiles under lupin–wheat rotation than under pastures.

The deposition and decomposition of plant residues do not cause subsoil acidification but contribute to the development of the soil pH profiles through the alkalization effect in the topsoil. Indeed, addition of plant residues to acidic soils has been demonstrated to increase soil pH. The magnitude of this pH increase (alkalinity production) in soil depends on the type of plant materials added, the rate of their breakdown, and the initial pH of the soil. Such alkalinity production was correlated positively with the concentration of ash alkalinity or excess cations in the residues [21,37,77] and negatively with the initial soil pH [21]. The increase in soil pH due to the residue addition has been attributed to (1) the decarboxylation of organic anions [78], (2) accumulation of NH_4^+ [79] and release of NH_3 during the decomposition of organic N [80], (3) production of OH^- by the ligand exchange between the terminal OH^- groups of aluminum and iron hydroxy-oxides and organic anions [81], (4) production of OH^- by reduction of Mn and Fe oxides under reducing conditions [81], and (5) an increase in soil base saturation through the replacement of protons and Al from exchange sites by cations coming out of the decomposed plant residues [82].

Although the extent of proton excretion from roots during plant growth is proportional to the root distribution, oxidation of organic anions during decomposition of the shoot residue mainly occurs in the topsoil because residues are generally not incorporated into deeper layers. Thus, the decomposition of shoot residues neutralizes the acid created during plant growth in the topsoil. In some soils where subsoil acidification has occurred, an increased soil pH with time of farming can be observed in the top layer. Root residues usually have less excess cations than shoot residues and have a lesser "liming" effect [21,77]. Therefore, root residue decomposition will not fully neutralize acidity created along the roots in the soil profile during the growth period, and acidity produced during growth will persist in the subsoil layers.

Although nitrification coupled with nitrate leaching is a major source of protons for topsoil acidification (see Chapter 2), it is not a cause of subsoil acidification because mineralization and nitrification of plant residue N occur mainly in the topsoil. For instance, 64% of N mineralization and 50% of nitrification in the soil profile of a loamy sand and 78% of N mineralization and 41% of nitrification in a sandy clay loam occurred in the top 5-cm soil layer [83]. Similarly, Young et al. [84] observed that nitrification was negatively correlated with soil depth in the surface 10 cm. Production of nitrate results in excess protons in the topsoil (where nitrification occurs). If the nitrate is taken up by plant roots in the topsoil, there is no net acidification. If the nitrate is leached, soil acidification then occurs in the topsoil layer. The uptake of the leached nitrate by plant roots in subsoil layers is accompanied by extrusion of OH^-/HCO_3^- and thereby reduces subsoil acidification [26].

Figure 2 summarizes possible causes of subsoil acidification. The acid produced during plant growth due to excess cation uptake makes a major contribution
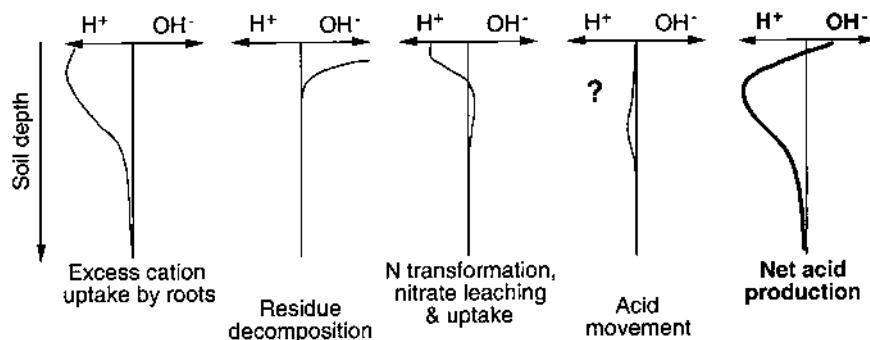
FIGURE 2 Schematic presentation of the possible mechanisms underlying the development of soil pH profiles.

to the development of the acidity profile. The amount of acid generated by plant roots is proportional to the root distribution. The oxidation of organic anions present in the residues, an alkalization process, however, occurs mainly in the topsoil and thus neutralizes only the acidity produced by plant growth in that layer. Therefore, the acidity in the subsoil persists. Leaching of nitrate that originated from nitrification of the residue N causes topsoil acidification. When leached nitrate is taken up in the subsoil, a portion of acidity generated by the root during plant growth is neutralized. Finally, the downward movement of H^+ and soluble Al [85], and NH_4^+ may potentially contribute to the development of subsoil acidification, but knowledge of the magnitude of leaching of these acidic components is meager at present.

5 MINIMIZING SOIL ACIDIFICATION THROUGH MANAGING CATION/ANION UPTAKE

This section provides some ideas on how acidification of soil, and especially subsoil, may be minimized through management of cation/anion uptake (see also Chapter 2). Detailed information on the amelioration of soil acidity by other means is covered in Chapters 11 and 12.

5.1 Maximize Nitrate Uptake

Whereas subsoil acidification appears to result mainly from excess cation over anion uptake by roots, nitrate leaching from topsoil is a major cause of topsoil acidification. In a grass–legume pasture, Helyar and Porter [2] estimated that the oxidation (mineralization and nitrification) of organic N and subsequent leaching of NO_3^- contributed to 40% of (top)soil acidification. Nitrate concentration can be as

high as 10 mM in the soil solution below 15 cm in sandy soils [5]. As discussed earlier, nitrate uptake by the plant is a deacidifying process. Thus, the efficient use of soil nitrate by plant roots in deeper layers during the downward movement of nitrate reduces subsoil acidification. The resultant topsoil acidification can easily be ameliorated by liming or through shoot residue decomposition.

Tang et al. [26] demonstrated that uptake in the subsoil of nitrate leached from the topsoil indeed decreased subsoil acidification under *Lupinus angustifolius, Trifolium subterraneum,* and *Triticum aestivum.* In 1-m soil columns where basal nutrients were applied uniformly throughout the column, root length density of the plants was relatively uniform below 10 cm. The addition of $(NH_4)_2SO_4$ in the top 10 cm increased NO_3^- concentration in all layers, but NH_4^+ was mainly retained in the top 30-cm layer. Compared with the N_2-fixing plants, the plants of *L. angustifolius* and *T. subterraneum* grown with $(NH_4)_2SO_4$ in 0–10 cm of the column caused more acidification in the top 10 cm but less acidification in the 10–50-cm depth. *Triticum aestivum* grown in columns with $(NH_4)_2SO_4$ in 0–10 cm increased soil pH below the 20-cm depth.

Plant species differ greatly in their ability to intercept NO_3^- as it is being leached down the soil profile. In the field, NO_3^- leaching was much greater under *Lupinus angustifolius* than under *Triticum aestivum* [86]. In a pot experiment with eight nodulated grain legume species (Fig. 1), increasing nitrate supply up to 57 mg N kg^{-1} soil increased nitrate uptake by 40 to 77% (the highest increase in *Lathyrus sativus* and the lowest in *Lupinus albus*). Accompanying an increase in nitrate uptake, proton excretion declined by 45 to 100% (the highest decrease under *L. sativus* and the lowest under *Cicer arietinum*). Genotypes within the same species may also differ in utilizing soil NO_3^- (e.g., genotypes of *Pisum sativum* [87]). Moreover, Bowman et al. [88] showed that less nitrate was leached under deep-rooted than shallow-rooted than shallow-rooted genotypes of *Agrostis palustris* (bentgrass) and suggested that root architecture (distribution and density) is important in uptake of leached nitrate in soil profiles. Selection of species and genotypes that produce acid the least and use soil NO_3^- to the greatest extent may provide an option for minimizing subsoil acidification. This would also reduce topsoil acidification if uptake of nitrate occurs in the topsoil.

Replacement of annual pastures with perennial pastures has a potential to reduce nitrate leaching. The nitrate leached under the pasture was reduced by half or more by establishing perennial grasses with *Trifolium subterraneum* [43]. Higher soil pH values have been measured under the *Phalaris*-based pasture than under a comparable annual grass/subclover-based pasture, with the net acid addition to the soil being 0.7 kmol ha^{-1} $year^{-1}$ lower under the *Phalaris* pasture [43].

Compared with acid-sensitive species, growing acid-tolerant species and genotypes on acidic soils usually leads to increased root growth, especially into acidic subsoils [89]. Such greater root density in the subsoil will increase the capacity of roots to absorb nitrate leached from the nitrification zone.

Subsoil acidification can be decreased through the management of N fertilizers. The application of nitrate fertilizers increased the pH of acid subsoils under perennial grasses [90]. More recently, Noble et al. [7] proposed that the formation of $Ca(NO_3)_2$ through the application of lime and NH_4^+-based fertilizers, subsequent nitrate leaching into, and the preferential uptake of NO_3^- in the subsoil offer a feasible and practical method for ameliorating subsoil acidity in sugarcane production.

5.2   Minimize Alkalinity Removal and Redistribution

Removal of any parts of the plant from the field will decrease alkalinity at the site and may cause permanent soil acidification. However, different plant parts contain various amounts of excess cations (see also Chapter 5). Leaves generally have a higher excess cation concentration than stem. Shoots have more excess cations than roots, which in turn have more than seeds [13,14,21,25]. The removal of seeds would therefore cause less acidification than removal of shoots. The acidifying effect of plant growth is greater when the plant is cut for hay or silage and the plant material removed than under a grazed pasture where the proportion of alkalinity returned in the form of animal excreta is relatively large [1].

As discussed earlier, legumes usually have a greater capacity to excrete protons and less ability to take up nitrate during growth compared with cereals. They also have higher excess cations or ash alkalinity in their tissues (Table 1) and thus higher amounts of alkalinity can be removed in their products. A decrease in the proportion of legumes in the rotation would thus reduce soil acidification. However, this is likely to have adverse effects on overall production and profitability in many agricultural regions because of a lack of input of N fixed by legumes. Alternatively, selection of legume species with low excess cations or ash alkalinity in the products is an option.

5.3   Impact of Trees and Shrubs

Trees and shrubs may play a role in minimizing soil acidification through the development of deep root systems capable of taking up bases such as Ca and Mg in deep layers of the soil profile and returning them to the topsoil as leaf litter containing excess cations or ask alkalinity. Furthermore, trees and shrubs, with their deeper rooting patterns and perennial nature, have a potential to capture more soil nitrate than crops and annual pastures, thereby reducing nitrate leaching and decreasing net acid input. It should be noted, however, that the decrease of acidity in the topsoil due to leaf litter decomposition is at the expense of increased acidification in the deep soil layer.

Excess cations or ash alkalinity in leaf litter of trees ranged from 36 to 247 cmol kg^{-1} [37]. Most eucalypt and acacia species and radiata pine had relatively low concentrations of ash alkalinity, whereas a number of northern hemisphere

deciduous species had higher ash alkalinity. *Milia azedarach* (white cedar), a native species of Australia's east coast, had the highest ash alkalinity among the 16 species tested. An addition of the leaf litter materials to an acid red podzolic soil increased soil pH and decreased extractable Al; the increase in pH was proportional to the quantity of excess cations or ash alkalinity added [37].

Information on the effect of trees and shrubs on decreasing soil acidification in the field is limited. A field survey showed that the soil under tree and shrubs was less acidic than adjacent soil and had higher exchangeable cations and lower extractable aluminum [91]. Growing *Chamaecytissus palmensis* (tagasaste) on an acid soil resulted in a rise in the soil pH beneath the shrubs [92]. However, the increase in pH diminished 2 m away from the shrub row (C. Tang, unpublished).

6 CONCLUSIONS

Excess uptake of cations over anions by plant roots plays an important role in soil acidification, especially in the development of subsoil acidity. Plant species and genotypes differ substantially in concentrations of excess cations or ash alkalinity and their ability to produce acid and to utilize soil nitrate. Soil acidification under legumes is greater than under nonlegume crops because of (1) large excess uptake of cations over anions due to N_2 fixation and (2) the low capacity to take up nitrate once organic N is decomposed. Ammonium nutrition increases and nitrate decreases soil acidification under other crops. Whereas much emphasis has been placed on the amelioration of soil acidity, more efforts should be devoted to minimizing or preventing soil acidification and, especially, subsoil acidification. Selection of species and genotypes with low excess cations in the products, low acid production, and high capacity to take up soil nitrate may provide an option to minimize subsoil acidification. Perennial species may also play a role in this respect. Further, strategic use of N fertilizers with minimal NH_4^+ leaching from the topsoil and maximal NO_3 utilization in the subsoil may be considered.

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4

Acid Inputs into the Soils from Acid Rain

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1 INTRODUCTION

Industrialized regions of the world have been confronted with the consequences of acidic deposition since the beginning of the 20th century. Today, there is substantial concern about the environmental impacts of air pollution on the local, regional, and global scale [1]. It has been shown that observed levels of various air pollutants can threaten human health, vegetation, wildlife, and soil biology; cause damage to materials; and change the chemistry of soils and waters.

The term "acid rain" or "acid deposition," which covers the wide range of physical, chemical, and biological processes involved in the issues of acidification, is defined here as the acid input to ecosystems and soils from the atmosphere originating in human activity (e.g., in fossil fuel burning). Although there is some question of whether any location on the earth is untouched by human activities in some way, the natural troposphere is usually referred to as the atmosphere over remote areas [2]. Thus, the anthropogenic pollution of the atmosphere, which is the origin of acid rain, always has to be assessed in comparison with the natural troposphere.

Widespread regulatory action to curb air pollution was not taken until strong links were established between human health and pollutants in the mid-1900s. Until the 1950s, air pollution was emitted from relatively short smokestacks and had

the most profound effects in areas immediately surrounding the source. In urban areas throughout the world, pollution events were both severe and frequent enough during this time period that they often led to human health problems [3]. One smog event in London in 1952 reportedly caused 4000 deaths [4]. In an effort to ameliorate the urban pollution situation, smokestack height was increased in North America and Europe between the 1950s and 1970s so that pollutants would disperse more widely. With the increased stack height, local pollution became regional pollution, and the era of the long-range transport of acid deposition had started. Acid rain problems have also extended to Asia because of a significant increase in atmospheric emissions resulting from high economic and population growth [5].

The deleterious effects of acid rain on soils have much in common with those of acid produced naturally in soils; the active principles, acids in solution, are similar [6]. However, anthropogenic atmospheric deposition was shown to influence the biogeochemistry of forest ecosystems significantly and to accelerate soil acidification [7,8].

This chapter gives an overview of the forms and the origin of acidifying pollutants as well as deposition processes and their measurements. A short section deals with the consequences of acid deposition for ecosystems and their biota. The chapter ends with a discussion of long-term trends and the expected changes in acid deposition in the future.

2   ORIGIN AND FORMATION OF ACIDIFYING AIR POLLUTANTS

Once emitted, many air pollutants remain in the atmosphere for some time before they are finally deposited on the ground. During this time, they are transported with the air mass over long distances, often crossing national boundaries. As a consequence, at a given site, the concentration of pollutants and their deposition on the ground are influenced by a large number of emission sources, frequently from many different countries.

The processes of atmospheric deposition are complex and involve several different mechanisms in forms of wet (rain or snow) and dry deposition (aerosols including fog and cloud droplets, absorption of gases on wet surfaces, and deposition of dust particles). The complex interaction with forest canopies or leaves of plants is discussed in Sec. 3. However, it is important to keep in mind that these interactions already take part in transforming deposited substances before they reach the soil surface.

In the following, the primary cause of acid deposition, the emissions of nitrogen and sulfur compounds to the atmosphere, resulting in the formation of nitric acid (HNO_3) and sulfuric acid (H_2SO_4) and the deposition of ammonium (NH_4^+), will be discussed. At the end of each section, a discussion of control tech-

niques and possible abatement strategies will be given. When discussing abatement strategies, it is important to keep in mind that North America as well as Europe has so far concentrated only on best available technologies to reduce emission of NO_x or SO_2. However, nontechnical options, such as substitution of fuels (e.g., switch from high- to low-sulfur coal or oil), substitution of the energy carrier (switch from coal to oil to gas or increased share of renewables), and rational use of energy, have a great potential to reduce emissions at low costs [9]. The latter abatement strategies might become especially important for Northeast Asia (see Sec. 5.3).

2.1 Nitrogen

For the global nitrogen budget, Galloway [10] estimates 140 million tons of nitrogen per year to be mobilized just by human activities (80, 40, and 20 million tons from commercial fertilizer production, legume and rice cultivation, and fossil fuel combustion, respectively). Of these 140 million tons per year, only 80 million tones are emitted to the atmosphere: 20 million tons from fossil fuel combustion and 50 and 10 million tons per year from agricultural activities as ammonia (NH_3) and nitrogen oxide (NO_x), respectively [10]. Because sources and sinks of NH_3 and NO_x differ significantly, they are discussed separately in the following.

2.1.1 NO_x

Nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O, known as "laughing gas") are collectively named NO_x. Other nitrogen oxides such as nitrogen trioxide (NO_3), dinitrogen trioxide (N_2O_3), dinitrogen tetroxide (N_2O_4), and dinitrogen pentoxide (N_2O_5) are also identified in the atmosphere, but they decompose to NO_2 by reacting with NO and/or by photolysis [11].

The NO_x gases enter the atmosphere from natural and anthropogenic sources. The main oxidized nitrogen compound emitted is nitrogen monoxide, which is oxidized to nitrogen dioxide. The oxidation of NO_2 by OH is the major route of formation of nitric acid in the boundary layer of the troposphere:

$$OH + NO_2 \rightarrow HNO_3$$
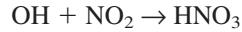
The N_2O gas is relatively unreactive; however, its concentration decreases rapidly with altitude as a result of a photochemical reaction yielding dinitrogen and monatomic oxygen:

$$N_2O + light \rightarrow N_2 + O$$
$$N_2O + O \rightarrow N_2 + O_2$$
$$N_2O + O \rightarrow NO + NO$$
$$NO + O_3 \rightarrow NO_2 + O_2$$
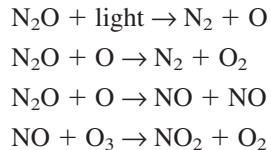
NO_x plays a considerable role in the production of ozone in the troposphere [12]:

$$NO_2 + h\text{v}(\lambda \leq 430 \text{ nm}) \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M \text{ (increased energy)}$$
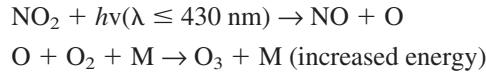
in which M is another species, such as a molecule of N_2 or O_2, which absorbs the excess energy of the reaction and stabilizes the ozone molecule. The reaction is an important primary photochemical process initiating smog formation because the monatomic oxygen or the ozone produced reacts with hydrocarbons to produce highly reactive hydrocarbon free radicals. The hydrocarbon free radicals react further with species such as NO_2 to produce peroxyacetyl nitrate, aldehydes, and other smog components.

The reaction sequence for O_3 production involves converting NO to NO_2 at a rate sufficiently high to maintain an NO_2/NO ratio to sustain the observed background levels of O_3 [12].

For the global NO_x budget, Logan [13] gives sources amounting to a total of 25 to 99 million tons N per year versus sinks (precipitation and dry deposition) of 24 to 64 million tons N per year. Of the sources, 40% is attributed to fossil fuel combustion, 22% to burning of biomass, 15% to lightning, 15% to microbial activity in soils, and 1 to 10% to the chemical oxidation of ammonia [13].

In Europe, the sector "public power plants cogeneration and district heating" contributes 21% of the total NO_x emission, 13% is produced by industrial combustion processes, and the remaining 65% is attributed to the transport sector [14,15]. Road transport accounts for the major part of the emissions from the transport sector (90%), with less than 3% from aviation and the remaining part from sea transport and inland waterways [15].

The most common approach in Europe and North America to reduce NO_x emissions is to define technology, fuel, and pollutant-specific emission standards for the most relevant sources. The NO_x emissions can be reduced by avoiding the formation of pollutants (primary measures) or by flue gas cleaning (secondary or end-pipe measures) [14]. Primary measures are based on lower combustion temperatures that lead to lower NO_x formation. A further reduction is achieved by integrated emission control measures such as air staging and flue gas recirculation [14]. Secondary NO_x techniques result in NO_x reduction by adding nitrogenous agents such as ammonia or urea, which react with the nitric oxides to form nitrogen and water. An important development was the catalytic converter for automobiles in which platinum catalyzes the reaction of NO_x to N_2 and CO to CO_2.

2.1.2 NH_4

Reduced nitrogen is present in the atmosphere almost entirely as gaseous NH_3 or particulate NH_4^+ (either solid or liquid droplets). Ammonia (NH_3) has a relatively short residence time in the atmosphere because it is rapidly converted to ammo-

nium (NH_4^+), thereby neutralizing acid pollutants (H_2SO_4, HNO_3, or HCl) in the air as well as in the water phase. Thus, the emission of ammonia is, strictly speaking, not a cause of acid rain. However, the conversion of NH_4^+ to either amino acids or NO_3^- in soils is always connected with the production of acidity. The assimilation of NH_4^+ during production of amino acids produces 1 mole of protons per mole of NH_4^+:

$$NH_4^+ + R—OH \rightarrow R—NH_2 + H_2O + H^+$$
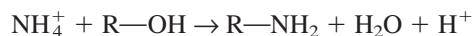
Nitrification of NH_4^+ to NO_3^- is connected with the production of 2 moles of protons for each NH_4^+ molecule:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

Furthermore, NH_4^+ deposition in ecosystems can cause substantial changes through eutrophication.

The main source of NH_3 is livestock farming (>90% in most countries [16]). The deposition of reduced nitrogen compounds is much more dependent on nearby point sources as nitrogen or sulfur oxides because of the short lifetime of NH_3 in the atmosphere [16] and the low emission height.

Estimates of total global NH_3 emissions are 109 to 131 million tons, of which 77 to 95 million tons are anthropogenically produced and 32 to 36 million tons are from natural processes [17]. Only around 10% of the anthropogenically produced NH_3 emissions are produced in North America and Europe. In Europe, the amount of N emitted as NH_3 is comparable to the amount emitted as NO_x (6.5 and 7.1 million tons, respectively [18]). In the United States, 1 to 3 million tons of N are emitted as NH_3 [19].

More than 40% of ammonia emissions in Europe result from intensive pig, cattle, and poultry production (housing and storage), 35% from applied manure, 3 to 17% from fertilizer, and the remainder from industry and households [19–21]. For the United States, approximately 65% is attributed to livestock waste, 10% to fertilizer application, and 25% to industrial processes [19]. For Japan, the overall total NH_3 emission from livestock was given as 12×10^5 tonnes NH_3 per year [22], which represents relatively small emissions compared with those of most European countries [22].

The main source of NH_3 within livestock farms is animal excreta. The conversion of feed N to animal product is often inefficient, and most of the N is excreted. A reduction of N in the animal diet or an increase in the efficiency of utilization of dietary N is one suggested means of reducing NH_3 emissions [20]. Techniques for the reduction of ammonia emission are mainly focused on reducing the NH_3-emitting area exposed to the air, reducing the NH_3 or NH_4^+ concentration in solution, or reducing the exchange of air above the emitting surface [20]. The various methods to reduce NH_3 emissions from animal houses (scraping slurry from the floor, adding water to the slurry, acidifying the slurry, implement-

ing filters in the ventilation system to clean the air) are not feasible because of either increased work time or increased costs [20]. Techniques to reduce NH_3 emissions from storage (covering slurry stores) or during application of slurry (using trail hoses or shallow injection) seem to be effective and feasible. There is a high rate of NH_3 loss from slurry immediately after field application (more than half of the total loss might occur during the first 6 days [23]). Thus, postapplication techniques (incorporation of slurry by ploughing or rotary harrow, irrigation with water or rain) must be brought into operation as quickly as possible if they are to be effective. Furthermore, the timing of the surface applications of slurry is important as losses are weather dependent. Because of the increase of NH_3 emissions with an increase in temperature, warm weather should be avoided. Unfortunately, this conflicts with the need for good trafficability of the soil and the desire for good crop-growing conditions.

Generally, the abatement strategies for NH_3 emissions are not easy to solve because of conflicts in economic interests and the side effects of some of the measures. For example, mixing deep litter in animal houses reduces NH_3 emission but causes high emission of the greenhouse gas nitrous oxide [24]. A further problem is the conflict with aiming at an environment beneficial to animals. For instance, tying animals during housing reduces the slatted floor area to which excreta is spread and has been shown to reduce NH_3 emissions by nearly 80% [24]. The latter conflict may be solved in some cases by increasing the proportion of the year during which the animals are allowed to graze, which would reduce the ammonia volatilization at the farm level and simultaneously increase economic benefits and animal welfare [20].

2.2 Sulfur

A number of gaseous sulfur compounds are emitted into the atmosphere through natural processes and/or anthropogenic activities. The most commonly known are sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS or OCS), dimethyl sulfide (CH_3SCH_3), methyl mercaptan (CH_3SH), carbon disulfide (CS_2), and dimethyl disulfide (CH_3SSCH_3) [11]. Of these, SO_2 is the dominant species (~95%) and of greatest environmental concern.

The largest part of the naturally emitted sulfur enters the atmosphere as H_2S [6]. The H_2S emitted into the atmosphere is converted to SO_2 within hours to days. The chemical reactions involved are complex but probably include free radical formation:

$$H_2S + O \rightarrow OH + HS$$

The overall reaction would be

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$
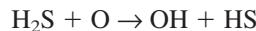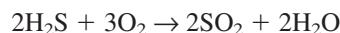
The greater part of the anthropogenically produced sulfur originates from burning processes; thus, it enters the atmosphere as SO_2. Once in the atmosphere, SO_2 is oxidized to SO_4^{2-} by homogeneous (gas to gas phase) or heterogeneous (gas to particle phase) reactions. The oxidation mechanism involves a complex photo-oxidation cycle (for details see Ref. 11), but according to Tanner [19] the principal gas-phase route for H_2SO_4 formation is

$$SO_2 + OH^- \rightarrow HSO_3$$
$$HSO_3 + O_2 \rightarrow SO_3 + HO_2$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

The overall reaction would be

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow H_2SO_4$$
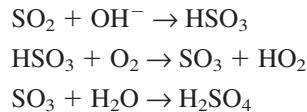
The reaction represents a series of steps of somewhat uncertain nature. Normally, the rate of conversion of sulfur dioxide to sulfur trioxide is very slow. However, sunlight in a humid atmosphere appears to catalyze the reaction, and NO_x is known to increase the rate of conversion.

A limited quantity of sulfates (SO_4^{2-}, SO_3^+, H_2SO_4) is directly emitted to the atmosphere by industrial processes such as petroleum refining, nonferrous smelting, pulp milling, and the manufacture of sulfuric acid [19].

It is estimated that, on a global scale, one half of the sulfur entering the atmosphere results from human activities, the other half from natural processes [25]. Each fraction approaches 100 million tons per year [26]. For the northern hemisphere, Cullis and Hirschler [27] give an estimation of 76 million tons in 1976 from natural sources versus 98 million tons from anthropogenic sources. For the southern hemisphere, they estimate 72 and 6 million tons for natural and anthropogenic sources, respectively [27].

The approximate percentage contributions of the main sources of natural sulfur emissions are as follows: volcanoes, 18%; open-ocean biogenic production, 46%; coastal zone and wetland biogenic sources, 3%; terrestrial plants and soils, 13%; biomass burning, > 4%; wind-raised dust, 16% [25]. Cullis and Hirschler [27] give 3% for volcanoes and approximately 30% each for open-ocean biogenic production, sea spray, and land biogenic production. However, it should be noted that the estimated ranges of natural sources are highly uncertain, mainly because of the extrapolation of a few point measurements to the global scale. Hence, the numbers given vary considerably.

The origin of anthropogenically produced SO_2 emissions differs in size between the continents. The approximate regional apportionment of fossil fuel sulfur emissions in 1980 was 16% for China and Japan, 28% for the United States and Canada, 34% for Europe, 15% for the remainder of the northern hemisphere,

and 7% for the southern hemisphere [28]. The main source of the oxidized sulfur from human activity is the burning of coal. The greater part of the world's coal used for energy burning contains more than 2% sulfur in the form of either pyrite (FeS$_2$) or organic sulfur [6]. In Europe, over half of the SO$_2$ emission in 1996 came from burning of fossil fuels, mostly in power plants [29]. The sector "public power plants cogeneration and district heating" contributes 54% of the total SO$_2$ emission, and 25% is produced by industrial combustion processes [14].

Despite the fact that SO$_4^{2-}$ deposition as well as SO$_4^{2-}$ concentrations in soil solutions and stream waters have been reduced considerably in northwestern Europe and eastern North America [30–34], determination of the source and fate of atmospherically deposited SO$_4^{2-}$ remains a critical issue for scientists and policy makers. Especially in Asia, concern about long-range transport of air pollution and the question of source–receptor calculations are matters of public and political concern between countries [35,36]. In the past, the origin of emissions was usually calculated by long-range transport models that can give only a broad regional perspective. Because stable isotopic values of S can serve as a "fingerprint" to identify S sources and trace their fates in the environment, several studies tried to link isotopic signatures to geographical or chemical origin. Most studies have found striking seasonality between summer and winter δ^{34}S values in precipitation in eastern North America with the summer samples being generally depleted in ^{34}S compared with the winter ones [37–40]. These studies concluded that the depleted ^{34}S values in the summer were due to higher emissions of biogenic S that is depleted in ^{34}S. Mixing models were used to calculate that the biogenic contribution to the SO$_4^{2-}$ deposition could account for up to 30% of the atmospheric S burden. However, other studies concluded that temperature and solar radiation effects as well as the marine aerosol contribution are responsible for seasonal patterns in δ^{34}S and biogenic emissions have been overestimated in the past [41–46]. Because the influence of anthropogenic SO$_2$ emissions on δ^{34}S values in precipitation is dependent on the fossil fuel usage of the area, Alewell et al. [46] tried to link stable isotopes to fossil fuel usage of source states in the northeastern United States. However, the high variability of the δ^{34}S values of various fossil fuels makes it difficult to use stable S isotopes for identifying whether changing fossil fuel utilization has affected the δ^{34}S values in bulk precipitation [46].

As for NO$_x$, the common approach in Europe and North America to reduce SO$_2$ emissions is to define technology, fuel, and pollutant specific emission standards for the most relevant sources. In addition, most countries have limited the allowed sulfur content of fossil fuels. Countries such as Germany, The Netherlands, Italy, and the Nordic countries have limited the sulfur content of heavy fuel oils to 1%, in certain regions even less [15]. In Norway and Sweden, the introduction of a tax on sulfur has resulted in even lower levels. Because sulfur is almost completely oxidized to SO$_2$ during combustion processes, only secondary measures (in this case flue gas cleaning) are relevant for emission reduction. Most

technologies are based on the reaction of SO_2 with alkaline agents added as solid or as a suspension of the respective salts [14]. In other techniques, SO_2 is oxidized catalytically to SO_3, which reacts with water to form sulfuric acid. As for NO_x, nontechnical options to reduce SO_2 emission (see earlier) have a great potential to reduce emissions at low costs.

3 DEPOSITION PROCESSES AND THEIR MEASUREMENT

3.1 Wet Deposition Versus Dry Deposition

In an open, uniform landscape, bulk deposition (the sum of wet and dry deposition) is measured by simple use of open precipitation collectors. However, this measurement is a fairly accurate estimate only for a homogeneous flat surface. For all other surfaces (e.g., canopies of forests), wet and dry deposition have to be measured separately.

Wet deposition includes particulate diffusophoresis, Brownian diffusion to cloud or raindrops, impact and interception by raindrops, solution and oxidation in droplets, and uptake by falling raindrops [11]. Wet deposition is usually measured by simple use of open precipitation collectors. In a more advanced technique (providing more correct measurements), precipitation collectors will be opened only with the beginning of rain, thus excluding dry deposition during nonrain periods. The latter devices are normally referred to as wet-only samplers.

The deposition of cloud and fog water is sometimes referred to as occult deposition [47,48]. It has been shown that the deposition of cloud and fog water is a considerable part of bulk deposition of SO_4^{2-}, NO_3^- and NH_4^+ [49]. Concentrations of major ions in cloud and fog water can be up to 25 times higher than in incident precipitation [49], and this has been suggested as one of the major factors leading to a decline in mountain forests in the Czech Republic and Germany.

Dry deposition leads to direct collection of gases, vapors, and particles on land, plant, and water surfaces. It can be broadly defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation [50]. The process of dry deposition involves three steps: turbulent transport from the free atmosphere to a relatively quiescent near-surface layer; boundary layer transport by convection, diffusion, or inertial processes; and chemical or physical capture of the chemical species by the surface [50,51]. The complexity of the individual processes involved and the variety of possible interactions among them already indicate the difficulties in measuring dry deposition. Dry deposition has been estimated to contribute up to half, or even more, of the total sulfur and nitrogen deposition in the northern hemisphere [11,50]. Thus, the need for correct measurement of dry deposition has often been stressed in the past [11,52].

There are no simple, direct measurements for quantifying dry deposition, but measurements can be divided into two categories. The first category, the sur-

face analysis method, examines the chemistry of exposed surfaces such as leaves or surrogate surfaces. This category includes foliar extraction, measurement of throughfall and stem flow (the difference between wet deposition above the canopy and the throughfall measurement below the canopy gives an estimate of dry deposition), cloud droplet collection, watershed mass balance (difference between input with wet deposition and total export yields in dry deposition), isotopic tracers, snow sampling (fresh snow is compared with old surface snow), and aerodynamically designed surrogate surfaces. Each of these methods has its problems. Foliar extractions rely on a large number of representative samples of the investigated surface. This is especially difficult when investigating heterogeneous forests with high canopies. The measurement of throughfall and stem flow in forest ecosystems is a relatively easy to implement, inexpensive method, which gives measurements over long time periods and integrates values measured across the canopy of trees. However, exudation or leaching from plant tissues can change element fluxes considerably, especially for nitrogen, potassium, and protons [53,54].

The watershed-mass-balance approach assumes that the total element input to a watershed is the sum of inputs by wet and dry deposition. Thus, subtraction of wet deposition from the total export from the system would yield dry deposition. However, internal soil pools acting as sinks or sources of elements might often be under- or overestimated by this approach [55,56]. Other surface analysis methods such as snow sampling, aerodynamically designed surrogate surfaces, or isotope tracers all have the problem of being representative for larger scales in space and time [50].

The second category for measuring dry deposition, the atmospheric flux method, infers fluxes from the atmospheric concentrations of the pollutants in question. This includes tower-based Eddy correlation, Eddy correlation from aircraft, Eddy accumulation, gradients method (measurements of contaminant concentration as a function of height), and the variance method (fluctuations in heat flux or humidity to estimate contaminant fluxes) (for detailed descriptions of the methods see Ref. 50).

A simplification of the formula used for the Eddy correlation would be

$$F = C \times V_d$$

with F the flux to the surface, C the atmospheric concentration, and V_d the deposition velocity.

Deposition velocities vary greatly between gases and as a function of meteorology and the nature of the surface. Thus, in the Eddy correlation measurement, the fluctuation of the vertical wind is measured with a fast-response airflow sensor such as a hot-film anemometer. The fluctuation of the concentration is measured with a sensor for the contaminant of interest. The flux measurements with Eddy correlation pertain to a spatial scale of several hundred meters upwind, with

a zone typically $\pm 15°$ from the average wind direction [50]. The main advantage of this method is that fluxes can be measured with reasonably high accuracy and good time resolution for ozone, SO_4^{2-}, NO, and NO_2. The disadvantage of the method is that the technique is accurate only in uniform vegetation with adequate fetch.

In general, atmospheric flux measurements offer certain advantages over surface analysis techniques, mainly that the flux estimates give data over a short period of time and that direct measurement of flux is possible. However, all atmospheric flux measurements require sensor and/or sampling equipment that may be expensive and not always reliable [50]. It is generally agreed that none of the methods in either category is useful for all situations and that a combination of techniques may be needed to maximize the quality of dry deposition data [11,50].

3.2   Throughfall Chemistry and Canopy Interactions in Forest Ecosystems

To estimate acid input to the soil in forest ecosystems, there is a need to consider canopy interactions for estimation of the total load to the soil. This includes the measurement of throughfall and stem flow. Throughfall is defined as the water dripping from forest canopies, and the term stem flow describes the water running down the trunks of trees. Nutrient transfer with throughfall and stem flow is usually substantially larger than that in incident precipitation. The alteration of the composition of water in contact with plant tissues may be attributed to both canopy interactions and atmospheric dry deposition. The measurement of throughfall has frequently been used to estimate dry deposition into forest ecosystems. The throughfall method clearly has the advantages of not being restricted to uniform surfaces or adequate fetches (see earlier) while at the same time including all gases and particles deposited at the surface of leaves. Furthermore, it is a fairly easy and inexpensive monitoring method. However, measurement of throughfall has been developed for quantification of element fluxes into forest soils and not for deposition estimates [21]. Physical (particle resuspension, evaporation, passive excretion of ions by diffusion), chemical (ion exchange, erosion of cuticular waxes by ozone or acidity, changes of membrane structure by either SO_2, acidity, or ozone), and biological processes (active uptake by higher plant foliage, active excretion by plant tissues, foliar H_2S emission, conversions by arthropods, active uptake by lichens and microepiphytes, release of dissolved substances by decomposition) influence the element composition in throughfall [54]. Throughfall fluxes are influenced by diffusion and exchange between the surface water and the underlying apoplast of canopy tissues [21]. Diffusion is the major cause of elevated anionic concentrations in throughfall, and both diffusion and ion exchange contribute to cationic concentrations in throughfall [54]. The rate of canopy exchange is dependent on the el-

ements considered as well as the tree species and ecological parameters. Coniferous trees loose less nutrients in the growing season than deciduous trees [21], but losses continue throughout the dormant season because conifers keep their leaves. Biotic stresses, such as canopy infestation by herbivore insects, can affect throughfall and soil solution chemistry, causing increased concentrations of dissolved organic carbon (DOC) and decreased concentrations of inorganic nitrogen throughout plague situations [57,58]. The amount and timing of precipitation are found to be relevant for canopy leaching: long residence times of the water during fog events or drizzle increase canopy leaching compared with events with large rainfall intensities.

For protons, up to 80% of the proton deposition may already be buffered in the leaves [59,60]. This fraction of deposited acidity reaches the soil not at the soil intersurface with the atmosphere but at the soil intersurface with the roots [60]. Estimation of the actual proton load to the soil is made even more difficult by the proton consumption and production during nitrogen turnover; the effective rate of proton load to soils by acid deposition can be assessed only if the transfer functions of NH_4^+ and NO_3^- are known [61]. Nevertheless, due to dry deposition effects, proton deposition with throughfall is in most cases still considerably higher than with wet precipitation only. For a detailed discussion of proton fluxes and concentrations in the rhizosphere, see Chapter 9.

It is beyond the scope of the present chapter to discuss interactions and processes for each element separately. Generally, canopies of the forests increase deposition rates considerably. By considering physical and chemical interactions and processes in the canopy, Matzner [53] gave estimates of wet and total deposition for a spruce and a beech forest ecosystem in the German Solling area at a time of high deposition rates (Table 1).

The generally lower rates in the beech compared with the spruce canopy are due to the loss of leaves (and thus decrease of surface) during the dormant season. The latter is especially obvious for the deposition of protons, where total deposition is twice the amount of wet deposition for the beech forest but four times for

TABLE 1 Estimated Rates of Deposition in Forest Ecosystems in the Solling (Lower Saxonia, Germany): Average Values 1969–1985 in kg ha^{-1} year^{-1}

Type	H	Na	K	Ca	Mg	Fe	Mn	Al	SO$_4$-S	Cl
Wet deposition	0.8	7.8	3.7	9.8	1.7	0.7	0.4	1.2	23.2	16.7
Total deposition, beech	2.0	14.1	6.6	17.1	2.9	1.3	0.7	2.1	50.0	32.5
Total deposition, spruce	3.8	17.0	8.0	21.1	3.9	1.6	0.9	2.5	83.1	38.6

Source: Adapted from Ref. 53.

the spruce forest. The same pattern holds true for the deposition of SO_4^{2-}, most of which is caused by the dissolution of SO_2 in the water films of leaves [53].

Total deposition of nitrogen to forest soils is difficult to measure because deposition is influenced not only by physical and chemical interactions but especially by biological processes. Considerable parts of the deposited nitrogen are assimilated in the canopy by plant leaves or microorganisms. Furthermore, nitrogen species can be converted in the canopy, e.g., from NH_4^+ to NO_3^- or N_{org}. A rough estimation by Matzner [53] for the Solling area gave canopy uptake of 7 kg N ha^{-1} year^{-1} for beech and 9 kg S ha^{-1} year^{-1} for spruce.

3.3 High Emission Rates Are Not Equivalent to High Deposition Rates

Because of the long-range transport of SO_2 and NO_x emissions, the regions or point sources that are the worst polluters do not necessarily receive the highest deposition rates. This phenomenon is frequently discussed and has become a political issue in North America, Europe, and Asia (see also Sec. 5 of this chapter). Although the highest emission rates of SO_2 in Europe are measured in central Europe, relatively high deposition rates are spread all over Europe and hit remote areas of northern Europe as well as regions of southern Europe. Highest SO_4^{2-} deposition was measured in the late 1970s and early 1980s, with up to 100 kg S ha^{-1} year^{-1} in the low mountain ranges of Germany and the Czech Republic [32]. A similar situation is found in North America. For instance, the Hubbard Brook Experimental Forest in a remote area of the White Mountains of New Hampshire receives relatively high SO_4^{2-} deposition from the states to the west and south with high emission rates (Illinois, Michigan, New Jersey, New York, Ohio, Pennsylvania, and Wisconsin [46,62]). However, it is noteworthy that deposition rates in North America are generally much lower than in Europe (only up to 17 kg S ha^{-1} year^{-1} [62]).

Because ammonia deposition is much more dependent on nearby point sources, spatial patterns of ammonia deposition normally parallel emission patterns. In Europe, high rates of ammonia emission have been measured generally in central Europe with maximum emission in The Netherlands, Belgium, southeast Germany, Austria, west Hungary, and west France (for maps see Ref. 63). Accordingly, most of central and eastern Europe has high ammonium deposition rates of up to 10 kg NH_4^+-N ha^{-1} year^{-1} and The Netherlands, Belgium, southeast Germany, and Austria have up to 20 and in some cases even 30 kg NH_4^+-N ha^{-1} year^{-1} [32,63].

4 CONSEQUENCES OF ACID DEPOSITION

The overall consequences of acidic deposition are definitely more than soil and water acidification. A brief discussion of the changes induced in soils and discus-

sion of the effects on forests and biota are given in the following. Other consequences are trace metal mobilization, damage to buildings, and impacts on human health. For further discussion of soil acidification due to acid rain see Chapter 2.

4.1 Soil Chemical Reactions Induced by Acid Rain

The question of the nature and extent of acidic deposition effects on soils is controversial [64], partly because the effects of acid rain on soils have much in common with those of acid produced naturally in soils [6,65]. In general, the following chemical reactions can take place after the deposition process: acid production, proton buffering (e.g., cation exchange), precipitation or dissolution of minerals, ion adsorption or desorption, formation of gaseous compounds, and reactions with the biota.

Once deposited, emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3) act as acidifying agents in soils and lakes. Several natural mechanisms (e.g., mineral weathering, deposition of alkaline dust) may neutralize a certain fraction of the acidifying deposition, depending on the type of the ecosystem and on a range of site-specific conditions (climate, hydrology, etc.). If acid deposition exceeds this natural absorption capacity, resulting changes in soil and water chemistry will cause damage to plants, soil organisms, and aquatic life. However, the monitoring of soil acidification induced by acid rain is difficult because of the long time frames involved [66] and the parallel development of natural acidification processes [65]. Both natural and anthropogenically driven soil acidification can result in extremely low base saturation, low pH, and low alkalinity [65]. One difference between natural and anthropogenically driven soil acidification is that anthropogenic soil acidification due to acid rain is connected to high soil solution concentrations of SO_4^{2-} and NO_3^- [65]. In contrast, the "acidifying anions" (referring to the anions responsible for proton and aluminum leaching) during natural acidification processes are organic anions and HCO_3^-.

In parts of northern Europe, forest soil pH has decreased by 0.5 to 1.0 units during the past 30 to 60 years, at least partly as a result of acidic deposition [67]. The deposition of nitrogen (NH_3, NH_4^+, NO_x) in ecosystems may contribute to eutrophication and changes in the function and stability of oligotrophic ecosystems (e.g., heathlands and bogs [67]). High nitrogen and/or SO_4^{2-} deposition has resulted in nitrogen and SO_4^{2-} accumulation in forest soils, leaching of base cations, and acidification of surface waters. For detailed discussion of element cycling in the processes of natural and anthropogenic acidification, see Chapter 3.

4.2 The Question of Soil Acidification and Forest Decline

Despite the lack of evidence for direct effects, there appears to be no doubt about the serious consequences of the complex known as acid rain in central Europe and northeastern America to forest ecosystems [68,69] (for a literature overview see

Ref. 64). More recently, serious effects of acidic precipitation have been recognized in China, particularly in the new industrial regions such as the Sichuan Province now exploiting extensive nearby coal deposits of high sulfur content [9,70]. However, the timing and magnitude of the forest response to environmental changes depend not only on acidification effects but also on a complex interaction between climate change, accumulation of atmospheric CO_2, and increased global mobilization of nutrients such as N and S [68]. Thus, direct empirical relationships between air pollution and forest decline were statistically hardly significant, even in such large monitoring studies as ICP forests in Europe (International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests [71]). However, Erisman et al. [72] attributed the lack of empirical relationships to a combination of the limited comparability of canopy condition data between countries, the large uncertainties in the derivation of environmental stress factors on the local scale, the neglect of several factors influencing canopy condition such as mechanical damage (e.g., wind break, snow break, fire) or biotic stress (insect attacks, fungi diseases, game and grazing, human activities), data availability, and interactions of air pollution with natural stress, age, and other tree characteristics. Furthermore, the relatively short time frame of the ICP forests program (1989 to 1995) did not take into account long-term effects of anthropogenic stress factors and did not allow time to improve methods.

Most countries in central and eastern Europe consider air pollution a serious threat to forest health [69]. During the annual forest survey in the summer of 1998, some 127,000 trees, spread over 5700 sample plots in a network covering most of Europe, were examined for defoliation. Of this number, 24% were assessed as damaged—meaning that they had lost more than 25% of their leaves or needles in comparison with reference trees of the same species [73,74].

In many areas, acid deposition to soils has increased leaching of base cations, leading to deficiency of nutrients, especially Mg and K [67]. Today, many forest soils of central Europe have low base saturation and low pools of exchangeable nutrient cations, especially of Mg [75]. The Mg-deficient nutrition of trees is a widespread phenomenon, estimated to affect up to 57% of the investigated Norway spruce sites in Germany [76]. The appearance of severe deficiency symptoms (yellowing of needles) was related to the exchangeable Mg in the soils and to decreased concentrations of Mg in soil solution [77–79].

Several studies concluded that soil acidification and increased N availability will decrease the fine root mass of trees and shift the rooting zone to upper soil layers or decrease root distribution altogether [67,80,81]. In combination with increased aboveground growth in many areas of Europe, which is most likely due to nitrogen addition, the root/shoot ratio will be decreased. This development will finally cause increase in drought susceptibility and destabilization of trees [81].

Besides loss of nutrient cations, the buffering of protons from deposition causes increased levels of Al in soil solutions that might have detrimental effects

on tree root growth and nutrient uptake [81,82]. In water culture experiments, the Ca/Al and Mg/Al ratios, rather than the Al concentration itself, largely determined the effect of Al on roots [82–84].

Cronan and Grigal [82] estimated the critical Ca/Al ratio in soil solution to be in the range of 1. Those observed in the Fichtelgebirge mountains (northeastern Bavaria, Germany) decreased to values as low as 0.3 in 1999 [79]. Jorns and Hecht-Buchholz [85] gave a critical value of the Mg/Al ratio in soil solutions as 0.2. The Mg/Al ratios as low as 0.08 have been reported for some German soils [79]. Deficiency of Mg is induced by ion antagonism, especially by high concentrations of H, NH_4, K, Ca, Mn, and Al [83]. Thus, high H and Al concentrations will definitely increase Mg deficiency symptoms. The implication of Ca/Al and Mg/Al ratios for the root activity under field conditions and for mature trees, however, is still debated [86]. Nevertheless, the Ca/Al and Mg/Al ratios are often used as an indicator of detrimental effects of soil acidification on trees and for the calculation of critical loads of acid deposition [86,87].

4.3   Acid Rain and Biota in Europe

A review of air pollution effects on European wild species has shown that fungi, mosses, lichens, higher plants, fish, mollusks, amphibians, and mammals are directly or indirectly affected by air pollution [88]. However, with many of the records, it is not possible to attribute the effect noted directly to one particular pollutant [89]. Most records refer to overall acidification effects, although in some regions (central and eastern Europe) acute multipollutant exposure (including heavy metal deposition) is likely to be an additional factor [88]. Some plant species have reportedly increased in numbers because of either enhanced nutrient availability (e.g., increased nitrogen deposition) or changes in community structure (e.g., acid-tolerant grass species are favored [67]). The latter can be caused by either loss of more sensitive species, thus creating a vacant niche, or physical changes in the habitat (e.g., canopy thinning causing increased light on the forest floor). The overall conclusions of Tickle et al. [88] suggest that air pollution and acidification have played a substantial role in population extinction in Europe. However, this conclusion can be applicable mainly to freshwater systems. Rhode et al. [67] have reported no known extinction of plant species in the terrestial systems, with only the effect on plant biodiversity.

The impacts of acidification on freshwater systems have been well characterized, and it can be concluded that acid deposition reduced alkalinity of lakes and streams [67]. In waters with a low buffering capacity, the pH can be reduced to levels that cause acute and chronic impacts on biological populations. An additional effect on biota is caused by increasing aluminum levels that accompany the lowered pH [67].

So far, most attention on national and international scales has been given to

higher plants, mosses and lichens, and animals rather than fungi, lower plants, or soil biota. Cause–effect relationships between acid deposition and soil biota have been investigated only in case studies. Generally, effects of acid deposition on soil biota are complex (for an overview see Ref. 90). Acid deposition causes species numbers and species diversity of soil fauna to decrease, partly owing to the increase in a few dominant species. Thus, acid deposition may affect competition between soil animals and thereby change the structure of soil animal communities [91]. The change in species composition contributes to a change in forest floor from more mull-like conditions (forest floor type with high biological activity and high turnover rates) to more moder-like conditions (forest floor with medium to low biological activity and turnover rates) [90]. Causal factors for the reaction of the soil fauna to acid deposition are direct sensitivity to protons or other chemical stress associated with acidification (decreased base saturation, reduced availability of cations, increases in aluminum, iron, or heavy metal concentration), change in reproductive success, alteration of the microflora composition, alteration of the chemical contents of leaf litter, changes in microhabitat characteristics (compaction of pore space with a change in forest floor), and shift in competitive relations and/or in predation pressure [90].

Over the next decade, the impacts of acidification and eutrophication in Europe and North America are foreseen to show a decrease, with a consequence of biodiversity showing some recovery. However, a full return to prepollution conditions is not to be expected because of changes in competition patterns and distribution of species. The introduction—whether voluntary or accidental—of species alien to European ecosystems or to other regions of Europe represents an increasing risk, favored by globalization of trade, exchange, and transports [92]. Thus, even if chemical parameters (e.g., nutrient status, acidity) returned to prepollution condition, indigenous species might not be successful in competing with well-established alien species. Furthermore, even while deposition of acidifying substances is declining, the expected growth of economic sectors such as transportation, manufacturing and other industry, recreation, and tourism will put additional stress on many ecosystems. This might prevent ecosystem recovery from acidification effects. Furthermore, genetic transfer between nonnative species, or possibly even genetically modified organisms, and indigenous species, genetic erosion, and isolation of species populations are likely to intensify over the next decade [92]. In summary, European ecosystems are confronted with a change in many environmental factors. Just receding acidification patterns might not help biological systems to recover.

When discussing effects of acid rain on biota, we should not forget that acid deposition can have a negative influence on human health. Increased concentrations of atmospheric S and N species can affect human health either directly (e.g., SO_2) or indirectly through ozone formation caused by NO_x emissions (see Sec. 2.1.1). In Europe, air pollution episodes of SO_2 may have resulted in up to 13,000

additional deaths per year [10]. Furthermore, the acidification of groundwater and drinking water supplies will be a direct human health hazard through high nitrate or metal concentrations (Al, Cd) released from the soils [67]. Furthermore, corrosion damage to drinking water supply systems can cause increased concentrations of Cu in drinking water. Other hazards, such as elevated concentrations of Cd in game or mercury in fish, have also been reported [67].

5 LONG-TERM TRENDS AND FUTURE DEVELOPMENT

This section discusses and presents historical trends, political programs regarding the reduction of anthropogenic deposition, and the deposition rates that can be expected in the future. Because deposition of pollutants is nearly always a sum of a large number of sources, mostly involving different countries [1,56], action to abate air pollution problems has to be coordinated internationally.

5.1 Europe

The hazards of acid deposition, mainly the relation between human health and smoke from coal burning, had already been addressed in the Middle Ages [21]. During periods of low wind speed and/or foggy conditions, the main industrialized cities in Europe experienced high concentrations of smoke, reducing the visibility and increasing the number of deaths each year [4]. From the beginning of the 20th century, emissions of sulfur, nitrogen, and protons showed a steady increase (with setbacks during the world wars and the oil crisis, Fig. 1).

Since the late 1970s and early 1980s, a decreasing trend in the amount of acidifying air pollutants has continued. According to the reports of the European
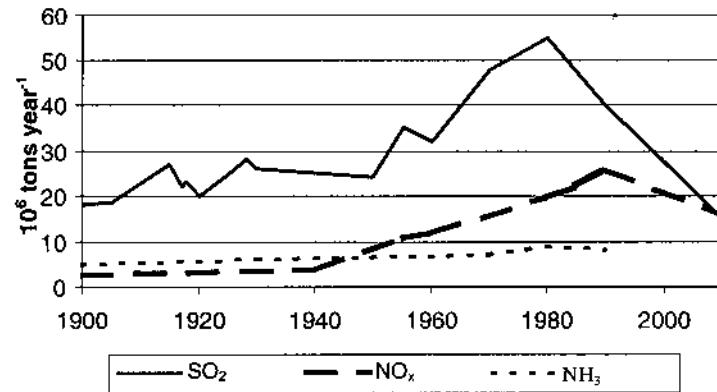
FIGURE 1 Long-term trends in gaseous emissions in Europe. (Data compiled from Refs. 29 and 21.)

Monitoring and Evaluation Programme [63], the total of Europe's sulfur emissions fell between 1980 and 1993 by more than 45%. By 1997, they were down by 60% [63]. Some countries, such as Austria, Finland, preunification West Germany, Norway, Sweden, and Switzerland, have cut down their sulfur emissions by as much as 75 to 80% between 1980 and 1997. Regarding NO_x emissions, European countries committed themselves only to ensure that 1994 emissions and beyond would remain below 1987 levels. However, several countries failed even that requirement [93], mostly due to growing prosperity and increased car ownership. Because of the time needed to replace existing vehicles with new ones equipped with catalytic converters, the full effect of these devices has yet to be felt. Still, the total European emissions of nitrogen oxides did fall by 10% between 1987 and 1994 [63]. The emissions of ammonia are estimated to have declined by 18% since 1980 [63].

In the 1980s and 1990s, the achievements in abating nitrogen emissions from stationary sources were almost counterbalanced by increased emissions due to more mobility, despite improvements in motor vehicle technology (for discussion of control techniques see Sec. 2 of this chapter). The European Union (EU) energy consumption is estimated to show a 17% increase from stationary sources and a 37% rise from mobile sources by 2010 [94]. In the agricultural sector, activity levels (livestock, nitrogen fertilizer use) are likely to fall, resulting in lower emissions [92].

The proportion of nitrogen deposited within the country of origin is far greater in the case of ammonia nitrogen than for oxidized nitrogen (see Sec. 2.1.2). Thus, a country will improve its own situation much more efficiently by reducing ammonia emissions [16], and a decrease in NH_3 emissions will be less dependent on international cooperation. This is especially important because differences between countries are distinct (e.g., The Netherlands use predominantly slurry-based systems in livestock production, whereas other countries use far more bedding and straw [16]) and an international abatement strategy is difficult to develop. Furthermore, different abatement strategies have very different efficiency values depending on system characteristics (e.g., climate, soil texture, slopes). Thus, a prediction of ammonia emissions in Europe is difficult to make. Whereas The Netherlands hope to reduce their ammonia emissions from agriculture by at least 50–70%, the overall maximum feasible reduction in Europe without radical agriculture reform is likely to be of the order of 30% [16].

The so-called multieffect protocol of the Convention on Long-Range Transboundary Air Pollution (LRTAP) became effective in December 1999 and was signed by 27 European countries [94]. Provided that the signatories to the protocol actually stick to the ceilings set and that emissions in the nonsignatory countries do not increase, the European emissions of sulfur dioxide, nitrogen oxides, volatile organic compounds, and ammonia may be expected to fall at least to the levels indicated in Table 2.

TABLE 2 Expected Emission Reduction (%) by 2010 from 1980 and 1990 Levels for the Present Members of the EU, the Non-EU Members (non-EU), and Both Together[a]

	Sulfur dioxide		Nitrogen oxides		Ammonia	
Location	1980–2010	1990–2010	1980–2010	1990–2010	1980–2010	1990–2010
EU	85	75	49	50	16	15
Non-EU	61	49	15	31	22	20
Europe	73	61	36	42	20	18

[a] Emissions from international shipping are not included.
Source: Ref. 94.

The sizable emissions of sulfur and nitrogen from international shipping are a matter that has usually been given little attention in Europe. However, emissions from shipping in the northeastern Atlantic and the North and Baltic seas will be equivalent to almost half of the total EU emissions of sulfur and more than a third of those of nitrogen oxides in 2010 [95] (see also Table 3). Use of sulfurous fuels in the shipping sector is not subject to any regulation, with the result that residual oils with a sulfur content of 3–4% are often used at sea [15].

The EU Acidification Strategy is targeting full protection of all ecosystems in the long term. Current interim emission targets for 2010 require reductions of 83% for SO_2, 55% for NO_x, and 29% for NH_3 compared with 1990 levels. However, these levels will not be achieved with existing and proposed policies [92].

When discussing long-term trends of acid inputs in European ecosystems, the "critical loads concept" is noteworthy. The critical loads concept is a first step

TABLE 3 European Emissions of SO_2 and NO_x in 1990 and 2010 in Million Tons

	1990		2010	
Source	SO_2	NO_x	SO_2	NO_x
EU countries	16.3	13.2	3.6[a]	5.9[a]
Non-EU countries	21.6	10.2	9.9[b]	7.3[b]
International shipping	1.6	2.3	1.6	2.3
Europe, total sum	39.5	25.7	15.1	15.5

[a] Projection in the European Comission's proposed directive for national emission ceilings.
[b] Projection in the multieffect protocol of the Long Range Transboundary Air Pollution Convention.
Source: Adapted from Ref. 95.

toward an effect-oriented pollution control, bridging the gap between scientists and policy makers [96]. The threshold "below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" is called the *critical load* [97]. For example, the threshold for terrestrial ecosystems was set by calculating the element concentrations in soil solutions for which no adverse effect on growth of trees and ground vegetation, soil stability, base saturation, and groundwater quality was to be expected [98,99]. For surface waters, indicator organisms were chosen for which the chemical limit is found and entered into mass balance models including all sinks and sources of acidity to estimate the necessary deposition reduction for N, S, and acidity [98].

In an effort coordinated by the UN/ECE Convention on Long-range Transboundary Air Pollution, all European countries estimated the critical loads for their domestic ecosystems. These national estimates were combined into a European critical loads database by the Coordination Center for Effects at the Netherlands Institute for Public Health and the Environment [100]. For the 1999 version of the critical loads databases, the number of countries that submitted the data has increased to 24. National focal centers have selected in total 1,314,806 ecosystems as receptors for calculating and mapping critical loads. Based on the two percentile criteria of the critical loads concept (i.e., the maximum deposition at which 98% of the ecosystems are protected), acid deposition will be greater than the critical loads in 24.7 and 4.3% for the years 1990 and 2010, respectively [1]. The critical loads concept has often been criticized because of its shortfalls (e.g., problems with summarizing geographical data, differences between methods of countries and regions, inflexibility of models not accounting for change over time, difficulties in defining achievable targets, defining clear thresholds, and multipollutant multireceptor problems [96]). However, despite these limitations, the critical loads approach has proved to be a useful practical tool for deriving pollution control strategies [96].

5.2 North America

Comparable to those in Europe, emissions of SO_2 and NO_x increased continuously in North America since the beginning of the 20th century. Yearly SO_2 emissions in North America had their maximum in the early 1970s, with over 30 million tons per year [21] (see also Fig. 2). Yearly NO_x emissions peaked in the mid-1980s. Concerns about the phenomena of transboundary flows of acid precipitation and their acidifying effects on ecosystems and hazards to public health led to the establishment of the Long Range Transport of Air Pollutants (LRTAP) program in Canada and the National Atmospheric Deposition Program (NADP) and the National Precipitation Assessment Program (NAPAP) in the United States. The Acid Rain Program of the U.S. Environmental Protection Agency (EPA) resulted in the Clean Air Act of 1995 [101]. Phase 1 of the Clean Air Act required the reduction of SO_2 emission in 1995 by 10 million tons below 1980 levels. The Clean Air Act
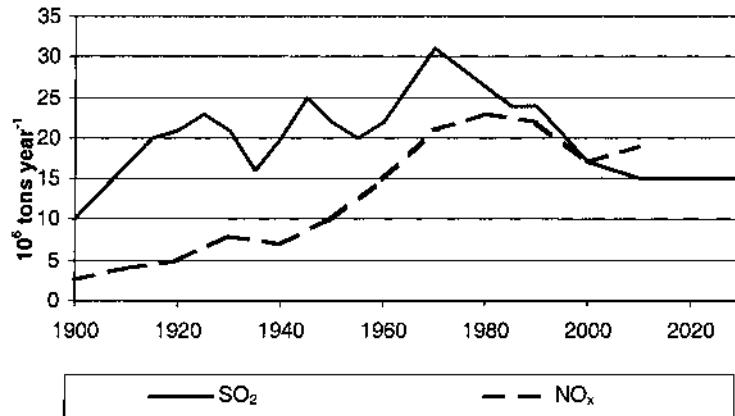
FIGURE 2   Long-term trends in gaseous emission in the United States. (Data compiled from Refs. 102 and 103.)

affected 445 mostly coal-burning electric utility plants, and the achieved reduction of SO_2 emissions in 1995 was 40% below required levels. A further reduction was required by the year 2000 (phase II). The Act also called for a 2-million-ton reduction in NO_x emissions by the year 2000 [101]. A significant portion of this reduction was to be achieved by coal-fired utility boilers that would be required to install low-NO_x-burner technologies.

Although SO_2 emissions are approximately two thirds of those in Europe and NO_x emissions are about equal, the deposition into the forest ecosystem is only a tenth to a fifth of that measured in European ecosystems. This is due to the different relationship of area and pollution source density in Europe and North America. Highest deposition rates in forest ecosystems in the northeastern United States peaked around 17 kg S ha^{-1} year^{-1} in the early 1970s [62,104]. Highest emission rates of SO_2 and NO_x in North America are found in the east, and especially in the northeast, of the United States [46].

Seasonal variation of SO_4^{2-} deposition is different in Europe and North America because of differences in fossil fuel usage. North America tends to have higher SO_2 emissions in summer due to extensive coal and oil burning to supply electricity for air conditioning, whereas energy for space heating is mainly supplied from natural gas. In Europe, anthropogenic SO_2 emissions are higher in the winter than the summer due to the combustion of fossil fuel for heat in the winter.

5.3   Asia

Northeast Asia is one of the most dynamic and diverse regions of the world. In contrast to North America and Europe, Northeast Asia is only starting to face

emissions problems. Fueled by high population growth and vibrant economies, energy consumption is currently 12% of the world's total and is projected to increase by a factor of 3 by 2020 [106]. According to Foell et al. [107], a "business-as-usual scenario" would increase the energy consumption in 2020 by about 3.5 times that of 1990. Because fossil fuels will provide much of this energy, emissions of sulfur dioxide are projected to increase by about the same factor (Table 4) [36,105,106]. Unless strong emission control measures are taken, Northeast Asia will face serious problems caused by increasing emissions in the next few decades. The SO_4^{2-} deposition in 1990 in various regions of China was already at 50 kg S ha^{-1} year^{-1} and reached peaks of 100 kg S ha^{-1} year^{-1} around the cities of Chonqinq in Sichuan Province [35]. The situation would already be much more serious were it not for the great quantities of neutralizing dust that are blown in from the desert areas in the west. The use of energy is expected to go on rising, particularly in the power generating and transportation sectors, as a result of booming electrification and a steadily increasing number of private cars [9]. Expected consequences in hard-hit areas (especially South Korea and the Chinese provinces Sichuan and Jiangsu) will be serious damage to crops, natural ecosystems, and human health [9].

Northeast China is the main emitting region (15 million tons SO_2 in 1990 [106]), and sulfur is transported across the Korean peninsula to Japan and beyond. However, there are serious efforts to improve the situation. Starting in January 2000, China has followed Japan in trying to improve air quality by making unleaded petrol with low sulfur contents widely available, setting the limits for sulfur in oil to 0.2%, and extending the natural gas network in the country [9].

TABLE 4 Emissions of Sulfur Dioxide in Northeast Asia in 1990 and 2020 According to Various Scenarios, in Million Tons of SO_2

Scenario[a]	Year	Northeast China	Japan	North Korea	South Korea	Asia, total
	1990	11.9	0.8	1.7	0.3	34
BAU	2020	32.5	1.1	5.5	1.4	110
BCT	2020	22.3	1.0	1.5	0.7	60
ACT	2020	17.4	1.0	1.5	0.7	NA[b]
BAT	2020	3.7	0.4	0.6	0.1	18

[a] BAU, business-as-usual scenario; BCT, basic control technology (modest emission control methods); ACT, advance control (only new point sources install state-of-the-art systems); BAT, best available technology (old and new point sources install state-of-the-art systems).
[b] NA, data not available.
Source: Adapted from Refs. 105 and 107.

Abatement technology for reducing emissions in Asia could cost USD 10 to 30 billion annually by 2030 and still provide only partial protection [95]. The costs for improvement in Northeast Asia according to the various scenarios may appear high, but they cover only technical measures, as do those in Europe and North America. However, there is a great potential for more efficient use of energy, which can reduce emissions at low costs [9]. From the European experience, international cooperation is the most effective means of emission control because of the transboundary movement of air pollutants. Furthermore, there are serious efforts to establish an acid deposition monitoring network in East Asia (participating countries are China, Indonesia, Japan, Republic of Korea, Malaysia, Mongolia, the Philippines, Singapore, Russian Federation, and Thailand).

In summary, acid deposition is evident today in Northeast Asia and will increase dramatically in the future. It is projected that severe damage to ecosystems will occur throughout the region without the introduction of emission controls. There is an urgent need for regional cooperation to improve the level of scientific understanding and develop a basis for region-wide control strategies [36].

5.4   Recovery of Ecosystems after 20 Years of Reduced Deposition in Europe and North America?

Even though deposition has been reduced in large parts of Europe, few signs of environmental recovery can be seen in Europe after 25 years of effort [92]. From a nature conservation viewpoint, Tickle et al. [88] conclude that new European pollution control measures agreed through the United Nations will not be sufficient to avert risk to key ecosystems, especially in countries such as Austria, Belgium, Denmark, Germany, Ireland, The Netherlands, Norway, Switzerland, Sweden, and the United Kingdom. Recovery of soil fauna due to beneficial effects of decreasing acid inputs has been reported only by Boxman et al. [108].

With respect to soil and water acidification, numerous studies in Europe and North America reported widespread aquatic recovery from acidification for European ecosystems due to the significant reduction of anthropogenic sulfate deposition [34,109–111]. However, overall conclusions may be biased because monitoring networks (e.g., ICP-waters in Europe) tend to focus on areas with high sensitivity to acid inputs. The high sensitivity is caused primarily by low storage capacity for sulfate and protons [soils that are characterized by all or a combination of the following parameters: (1) shallow postglacial soil development, (2) sandy soil textures, and (3) a high humus content]. Data for soils with a high storage capacity for sulfate and protons indicate that reversibility of water acidification can be delayed for decades because the release of previously stored sulfate causes cation leaching and acidification of deeper soil layers and waters. Studies from numerous regions of Germany (Solling, Spessart, Frankenwald, Fichtelgebirge, Bayerischer Wald, Schwarzwald) or the Czech Republic reported continu-

ing low pH and low alkalinity in streams or even an increase in groundwater sulfate concentrations [112–117]. In all studies, this delay in recovery was attributed to release of previously stored soil sulfate. Experimental manipulation as well as modeling scenarios with an 80% deposition decrease indicate for all types of soils in Sweden some recovery from acidification effects in the short term, followed, however, by very slow change thereafter [118].

One of the main problems connected to soil and water acidification is the leaching of nutrient cations (Ca^{2+}, Mg^{2+}, K^+) from soils. Due to a substantial reduction in particulate emissions within the past 20 years, the nutrient cation concentrations in throughfall and precipitation have declined in some regions. However, nutrient cation concentrations in stream waters did not always decline [113]. The latter is due to continued high SO_4^{2-} and NO_3^- concentrations in soil solutions and streams that are accompanied by high cation leaching. Even though high concentrations of nutrient cations in streams were usually interpreted as recovery of waters because of the increase in alkalinity [109,119], they result in a long-term export of nutrients and can point to a continuing (or even increasing) net acidification of soils [77,113]. In this context, it is important to note that an alkalinity increase in streams does not necessarily indicate a reversibility of soil acidification, nor does it indicate biological recovery of the streams so affected.

A significant delay of recovery from acidification in numerous regions of Europe and North America has important implications for water authorities, forest managers, and policy makers. Forest management is still confronted with the need for frequent liming to avoid depletion of soils and subsequent nutrient deficiencies in trees [77]. Water authorities should be aware that for waters (and thus drinking water supply) that drain areas containing soils with a high sorption capacity for sulfate, recovery of aquatic systems will be delayed for decades. Policy makers should consider that nitrogen deposition has to be reduced considerably in order to limit both cation depletion from soils and the further acidification of waters.

6 CONCLUSIONS

Regarding acid rain, industrialized regions of the world show very different trends for future development of sulfur, nitrogen, and proton deposition. Although in Europe as well as North America a significant decrease in sulfur and proton but only a slight decrease in nitrogen deposition can be noted, Northeast Asia is only starting to face the deleterious problems of acid rain. Because of the long-range transboundary transport of emissions of SO_2 and NO_x, international cooperation (in case of the United States, national cooperation between states) has been the only successful way to apply abatement strategies. It can be concluded that reductions in sulfur emissions in North America and Europe were achieved because of available technical options. In contrast, abatement strategies for nitrogen emissions

rely mainly on changes in human behavior (e.g., less motor vehicle use, consuming less meat to reduce livestock numbers) and energy use (e.g., more usage of wind, solar, and water energy; energy-saving strategies). Thus, a decrease in nitrogen emissions has been less successful so far. The good news for ammonia abatement strategies is that countries will directly benefit from their own efforts because there is hardly any long-range transport involved. Thus, there is hope for the future that site- and country-specific abatement strategies will be brought into action without the decades of delay connected with international political cooperation.

Scientific proof of the detrimental effects of acid rain on biota or soils is not easy to give. However, there is plenty of evidence that acid rain causes soil and water acidification, is connected to forest decline, has a negative effect on biodiversity, has a detrimental effect on human health, and can even cause extinction of plant and animal species.

Recovery from the deleterious effects of acid rain after 25 years of decreased sulfur and proton deposition in Europe and North America is up to now reported only for the reversal of chemical trends in aquatic systems. However, biological recovery (recovery of trees, aquatic species, etc.) as well as reversal of soil acidification has been noted to a minor extent only.

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5

Quantifying the Acid Balance for Broad-Acre Agricultural Systems

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1 INTRODUCTION

Soil acidification is a natural process that is accelerated by agricultural production [1,2]. It has been estimated that 80–90 million hectares of land in the agricultural areas of Australia are acidic, with 30–35 million requiring immediate remedial action [pH $(CaCl_2) < 4.8$] [3,4]. In Western Australia alone, two thirds of the soils in the agricultural areas of state are acidic or at risk from soil acidification [pH $(CaCl_2) < 5$].

Acid soils can be treated easily and relatively inexpensively using neutralizing agents such as lime (see Chapter 11). However, it is difficult to determine lime rates because acidification occurs slowly, and rates of acidification are hard

to measure [5]. These factors, combined with poor awareness of the extent of the problem of acid soils, meant that total use of lime and dolomite in Western Australia was only 117,000 tonnes in 1989–1990 [1]. Despite the extent of acid soils in the state, this had only increased to 177,749 tonnes across 11,300,000 ha of agricultural land under crop or pasture in 1995–1996 [6]. A large research and extension project was initiated in 1996 to increase awareness of soil acidity and liming and to investigate the effects of liming on other components of the production system. A decision aid for estimating net acidification rates (in terms of lime equivalents) for agricultural production systems in Western Australia was produced as part of the project.

This chapter describes the development of the decision aid just mentioned. Although the data presented here specifically apply to the production systems in Western Australia, the approach is valid for any location and production system. Calculated acidification rates using this decision aid are compared with estimates made using soil surveys.

2 QUANTIFYING THE COMPONENTS OF SOIL ACIDIFICATION

The processes that acidify soils [removal of produce (imbalance between cation and anion uptake), accumulation of soil organic matter, leaching of nutrients and fertilizer reactions] are well defined (see Chapters 2 and 3). It can be useful to think of acidification of soils under an agricultural system in terms of the contributions from each of these sources (Fig. 1). Net additions to a "pool" of acid occur when products are harvested, organic matter is accumulated, nitrate derived from the nitrification process in soil is leached, or acidifying fertilizers are applied. An estimate of the amount of acid added to the soil profile of a paddock or field over a year of production can be obtained from the sum of these processes. This in turn can be used to estimate the lime requirements (quantity of lime needed to neutralize the acid added) for different rotations.

We used this approach to estimate the acidification rates of soils in Western Australia under various agricultural rotations. The contribution of each of the major components was determined mathematically and then presented in the form of a simple decision tool for use by farmers and advisers.

2.1 Product Removal

Nutrient cycles are broken when alkaline produce is removed from the original site of nutrient uptake by the plant (see Chapter 2). The amount of acid added to a soil due to product removal is equal to the alkalinity of the produce removed from the system. This can be determined by measurement of the alkalinity of the ash following incineration of the product. Because plants extrude protons during up-
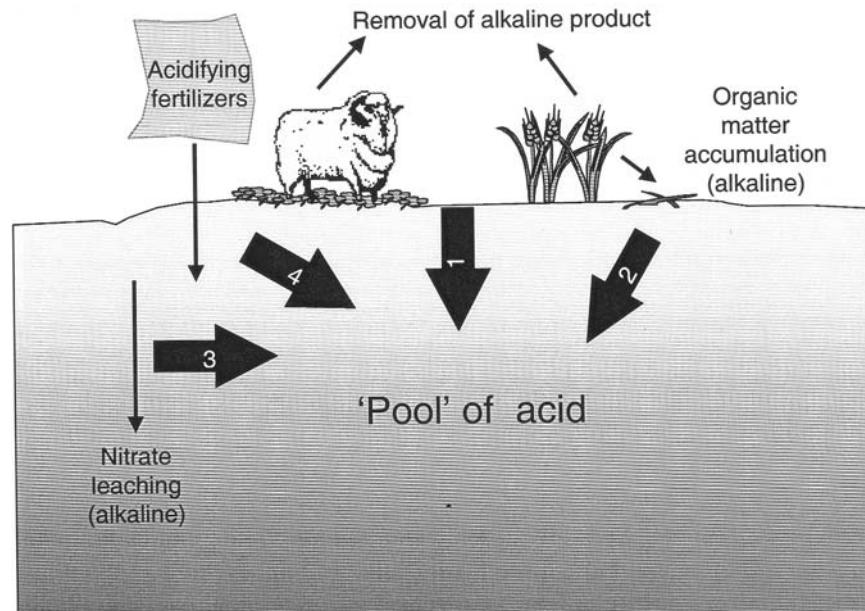
FIGURE 1 Schematic representation of the main sources of acidification of agricultural soils.

take of cations and extrude alkaline bases or hydroxyl ions in exchange for anions taken up, ash alkalinity can be estimated from the excess of nonnitrogen cations over anions in the product [1,2,7,8]. We estimated the acidification due to product removal in this manner.

A database of the content of all major plant nutrients in over 13,000 samples of seed and other plant parts analyzed from field research conducted in Western Australia was compiled. In combination with published information [9–20], these data were used to determine the average quantities of nutrients in various agricultural products. For animal products (beef, lamb, and wool) the deposition of feces and urine in nonproductive areas, such as stock camps and laneways, was also taken into account. Average concentrations of nutrients in the feces and urine of cattle and sheep and the quantity excreted per day were estimated using a range of sources [21–24]. Twenty-two percent of the excreta from sheep were assumed to be deposited in nonproductive areas of a paddock [25]. This amount was estimated as 0.9% for cattle.

The alkalinity of each product was determined from the difference between the sum of the cations and anions on an equivalent charge basis (charge/atomic weight). This was then expressed in terms of the removal per tonne (for crops) or

TABLE 1   Examples of the Equivalent Acidity Resulting from the Export of Various Agricultural Products[a]

Product	Acidity (kmol H^+ t^{-1} or kg^{-1})	Sample yield (t ha^{-1} or kg ha^{-1})	Lime equivalent (kg $CaCO_3$ ha^{-1})
Barley grain (*Hordeum vulgare*)	0.06	2.5	7.5
Canola seed (*Brassica napus*)	0.03	1.3	1.9
Chickpea seed (*Cicer arietinum*)	0.26	1.2	15.6
Lupin seed (*Lupinus angustifolius*)	0.3	1.4	21
Wheat grain (*Triticum aestivum*)	0.05	3	7.5
Wool (greasy)[b]	0.02[c]	20[c]	20[c]

[a] Values calculated from the sum of cations minus anions. Examples are also given of the lime requirement to neutralize the acidity for sample yields of each product. These figures were used in the Lime and Nutrient calculator.
[b] Includes estimate of removal of excreta to stock camps.
[c] Values per Kilogram.

per kilogram (for animal products) of produce. This was termed the *product removal number.* The acidification of the soil due to product removal was then calculated by multiplying this value by the quantity of the product that was harvested (Table 1).

2.2   Accumulation of Organic Matter

The accumulation of soil organic matter results in the breaking of nutrient cycles and thus contributes to the acidification of soils in a similar manner to the removal of alkaline produce [26]. Because there is little accumulation of organic matter in the old, highly weathered soils that support the extensive agricultural systems of Western Australia [27,28], this component was ignored in our calculations. Future decomposition of organic matter will generally have a liming effect, depending on the nitrogen content and alkalinity of the organic matter [29,30]. Therefore, it was considered that any accumulation of organic matter in the short term would be negated by the liming effect from the decomposition of crop residues in the long term.

2.3   Nitrate Leaching

Acid is produced during the formation of nitrate following the complete mineralization of soil organic matter, plant residues, and ammonium-based nitrogen fertilizers. In a complete cycle, this acid is neutralized by organic anions extruded by

the plant in exchange for nitrate taken up. However, because most of the mineralization occurs within 5 to 10 cm of the surface of the soil [31–34], the topsoil is acidified if the nitrate is leached to a point lower in the soil profile before it is taken up by the plant (see Chapter 3). This results in localized acidification, but there is no net acidification of the soil profile due to the organic anions that are extruded when the nitrate is taken up by the plant deeper in the soil.

Leaching of nitrate beyond the root zone of the plant results in net acidification of the soil. In this case the nitrate is too deep in the soil to be taken up by plants, so there is a net addition of acid to the profile due to the acid produced during the mineralization process. In our calculations we considered only nitrate leached beyond the root zone as we were calculating the acidification of the entire soil profile on an area basis.

Few studies have measured the leaching of nitrate under field conditions. In the past, the contribution of nitrate leaching to acidification has been estimated by difference using the method of Helyar and Porter [1]. Acidification rates were determined from pH measurements in cleared and uncleared sites [1,5,35–39]. The contributions to acidification due to the use of acidifying fertilizers and the carbon cycle components (product removal and accumulation of organic matter) were obtained from farm records, measurements, or the literature [40]. The contribution of nitrate leaching to acidification was then estimated as the difference between (1) the product of the measured acidification rates and the pH buffering capacity of the soil and (2) the sum of the contributions of the other components of acidification. This method can have large associated errors, particularly with the measurement of pH buffering capacity [27,28,41].

Anderson et al. [42] measured leaching of nitrate from a sandy soil in the medium- to high-rainfall zone of Western Australia (average rainfall 460 mm per annum). We used these measurements to estimate the quantity of nitrate leached per millimeter of annual rainfall under various crops. The estimated quantities of nitrate leached in each of the rainfall zones of the state were derived by multiplying the quantity of nitrate leached per millimeter by the average rainfall for the particular zone. This was termed the *leaching potential.*

The effect of soil texture on nitrate leaching (which was termed the *leaching intensity*) was estimated on the basis of broad definitions of soil type. Because Anderson and his colleagues measured nitrate leaching in a sandy soil, a "sand" was defined as having a leaching intensity (i.e., a multiplication factor) of 1. A "loam" was defined as having a leaching intensity one half that of a sand, and a "clay" was assigned a leaching intensity of 0.2 (J.W. Bowden, personal communication).

The estimated quantity of nitrate leached was determined from the product of the leaching potential and leaching intensity for all combinations of the three soil types and four rainfall zones for four categories of crops (Fig. 2). These quantities were comparable with the experiences of local researchers (J. W. Bowden
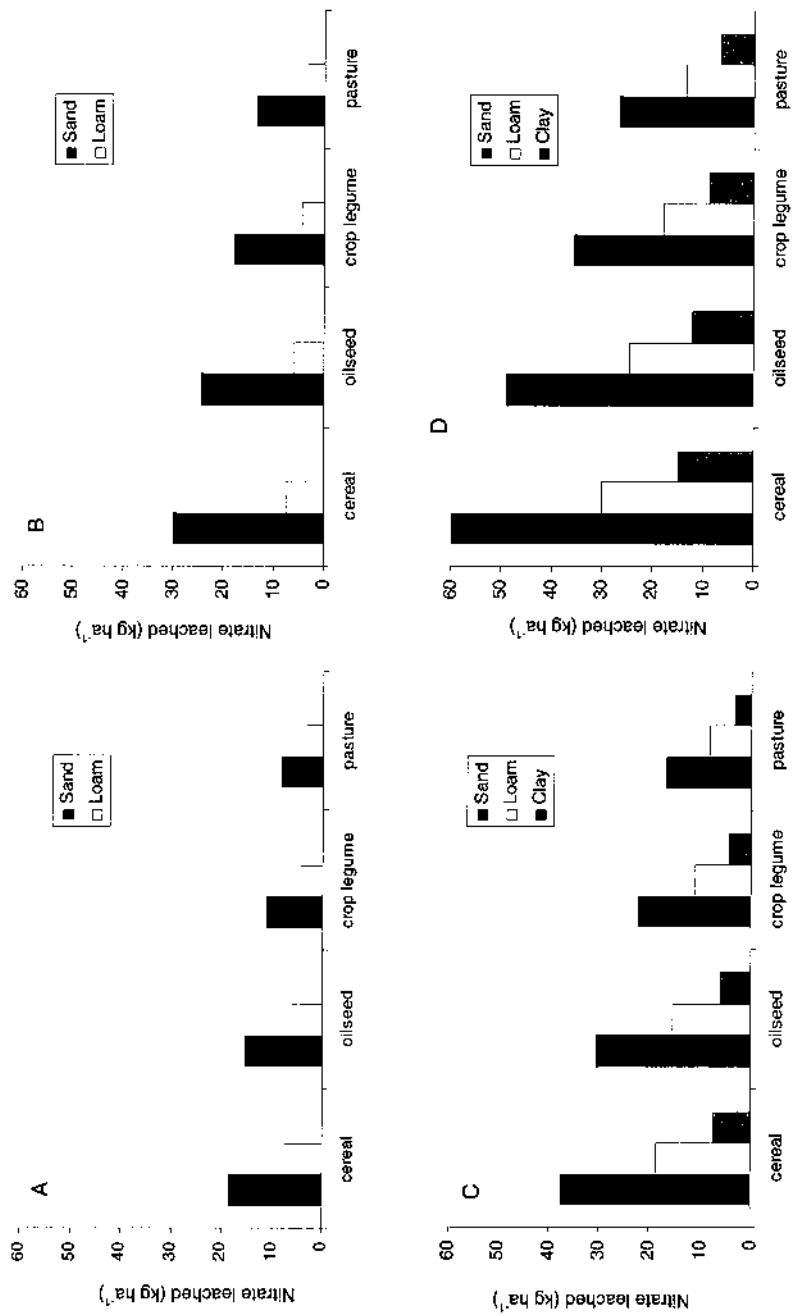
FIGURE 2   Estimates of the amount of nitrate leached under cereal, oilseed, and legume crops or pastures growing in a "sand," "loam," or "clay" soil in the 250 to 325 mm (A), 325 to 450 mm (B), 450 to 750 mm (C), and over 750 mm (D) rainfall zones of Western Australia. Values calculated using the Lime and Nutrient calculator. Note leaching on clay soils in zones (A) and (B) is zero.

and P. J. Dolling, personal communication) and with estimates obtained using a simulation model, the Agricultural Production Systems Simulator (APSIM) [43]. The majority of the nitrate leached from agricultural systems in Western Australia occurs over the summer–autumn period, before winter annual crops are sown, and early in the winter, when crops are just beginning to emerge [44]. The estimated quantity of nitrate leached under cereal crops reflects this asynchrony between demand and supply, particularly with the supply of nitrate derived from soil and residue sources.

It is important to note that for these estimates, the quantity of nitrate leached during the year was apportioned to the current crop. This is not strictly correct because the quantity of nitrate leached depends on both the amount of nitrogen left by the preceding crop (from fertilizer, soil and residue sources) and the nitrogen uptake by the current crop [45]. However, it was used here for simplicity in budgeting.

2.4 Acidifying Fertilizers

Fertilizers containing ammonium-based nitrogen compounds or elemental sulfur acidify the soil irrespective of any leaching of nitrate (see Chapter 2). Values for the acidification resulting from these compounds were derived from equations in Tisdale and Nelson [46] and Kennedy [47] (Table 2). The amount of acid added to the soil after application of a particular fertilizer will depend on the type and proportion of compounds that are used in the formulation of the fertilizer. This can be derived from the chemical formulation of the fertilizers, which, in our case, was kindly supplied by the respective fertilizer companies in Western Australia. The

TABLE 2 Amount of Acid Added to the Soil Following the Addition of Various Types of Nitrogen and Sulfur Fertilizers[a]

	Per kg of nitrogen or sulfur[b] in fertilizer	
Fertilizer component	kmol H^+	Lime required (kg $CaCO_3$)
Ammonium sulfate (AS)	1	3.6
Diammonium phosphate (DAP)	0.5	1.8
Monoammonium phosphate (MAP)	1	3.6
Urea	0	0
Calcium ammonium nitrate (CAN)	−0.2	−0.7
Elemental sulfur	2[b]	3.1[b]

[a] The quantity of lime required to neutralize the acid produced is also given. Negative values for CAN, which is a mixture of ammonium nitrate and lime, indicate a liming effect from this product.
[b] Values indicated are per kilogram of sulfur.

acidification was expressed per unit of nitrogen (or sulfur), termed the *fertilizer number.* The acidification resulting from any application of a fertilizer can be determined by simply multiplying the fertilizer number by the amount of nitrogen (or sulfur) applied as that fertilizer.

2.5 The Model

The contribution to soil acidification from the three components described previously was incorporated into a decision support tool, the Lime and Nutrient calculator [48]. The calculator estimates the amount of acid added to the soil (expressed as lime equivalents per hectare) following different rotations. Information about the crop grown, the yield, rainfall, and soil type is entered into the calculator, and an estimate of the total amount of lime equivalents removed per hectare is given by summing the contributions from each component. The calculator was produced both in a printed form, comprising a series of dials, and as a computer spreadsheet. Information on 15 agricultural crops and products was included.

3 ESTIMATING SOIL ACIDIFICATION FOR CROP SEQUENCES

3.1 Calculated Acidification Rates

Sequences of winter annual crops in Western Australia commonly consist of a cereal, typically wheat (*Triticum aestivum*), interspersed with a legume, such as lupin (*Lupinus angustifolius*), and another crop, such as canola (*Brassica napus*). We estimated the acidification rate for such a sequence of crops to illustrate the use of the calculator and the relative importance of the three components described earlier.

In this example, we considered the crop sequence lupin–wheat–canola–wheat grown on a sandy soil in the medium rainfall zone (325 to 450 mm) of Western Australia. The acidification rates were estimated at three levels of productivity, representing average yields and levels 30% above and below that figure (Table 3). The fertilizer rates and mix of fertilizers reflect those likely to be used at each level of productivity.

Predictably, the total acidification rate and average quantity of acid added per year increased with the level of production (Table 3). This increase was attributed to the higher yields (hence greater export of alkaline produce) and, at the highest level of production, to the use of acidifying fertilizers (Fig. 3). In all three cases, leaching of nitrate was the main factor contributing to acidification. This was the same for all levels of production due to the simplified way in which it was estimated by the calculator, but this in part reflects the asynchrony between nitrate supply from mineralization and plant demand.

Tools such as the Lime and Nutrient calculator are particularly useful for ex-

TABLE 3 Estimated Acidification Rates for a Lupin–Wheat–Canola–Wheat Crop Sequence "Grown" on a Sandy Soil in the Medium Rainfall Zone (325–450 mm) of Western Australia[a]

	Acidification rate		Crop, grain yield, and N fertilizer			
Production	kmol H^+ ha^{-1}	kmol H^+ ha^{-1} $year^{-1}$	Lupin	Wheat	Canola	Wheat
Low	7.8	1.9	1.1 t ha^{-1}	1.6 t ha^{-1}, 20 kg ha^{-1} urea	1 t ha^{-1}, 30 kg ha^{-1} urea	1.3 t ha^{-1}, 30 kg ha^{-1} urea
Moderate	8.0	2.0	1.5 t ha^{-1}	2.3 t ha^{-1}, 50 kg ha^{-1} urea	1.3 t ha^{-1}, 60 kg ha^{-1} urea	1.9 t ha^{-1}, 60 kg ha^{-1} urea
High	9.6	2.4	1.9 t ha^{-1}	3 t ha^{-1}, 50 kg ha^{-1} urea, 50 kg ha^{-1} DAP	1.7 t ha^{-1}, 60 kg ha^{-1} urea, 50 kg ha^{-1} amm. sulfate	2.5 t ha^{-1}, 60 kg ha^{-1} urea, 60 kg ha^{-1} DAP

[a] Rates were calculated at three levels of productivity (low, moderate, and high) using the Lime and Nutrient calculator. The yields are typical for this environment. Fertilizer applications are appropriate for the levels of production.
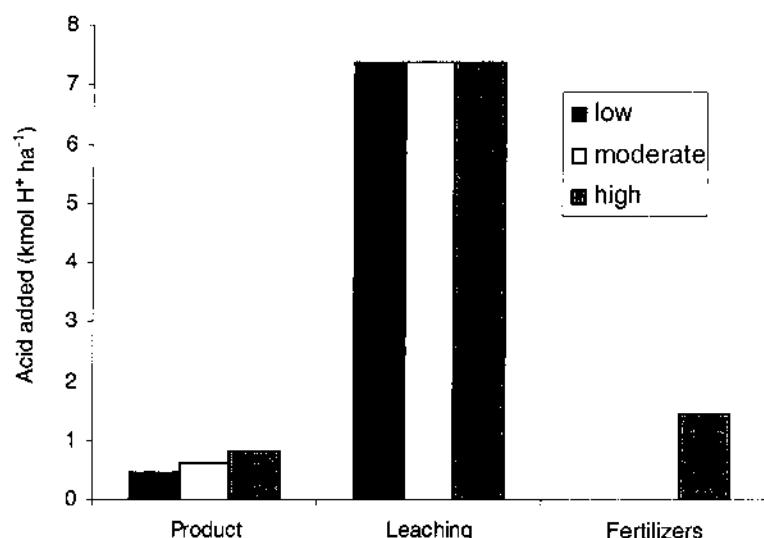
FIGURE 3　Estimated acidification rates for three levels of productivity (low, moderate, and high) of a lupin–wheat–canola–wheat crop sequence "grown" on a sandy soil in the medium rainfall zone (325 to 450 mm) of Western Australia. The results are presented as the average quantities of acid added by the three components of acidification (removal of alkaline produce, nitrate leaching, and use of acidifying fertilizers). Rates were calculated using the Lime and Nutrient calculator.

amining the likely impact of changes in management on rates of acidification, so-called what if analyses. For example, in the previous calculations, what would be the effect of changing the type of nitrogen fertilizer used? The rates of acidification at the highest level of production were reestimated using three types of fertilizer: DAP (diammonium phosphate), ammonium sulfate, and CAN (calcium ammonium nitrate), which respectively represent moderate, high, and low acidifying fertilizers (Table 4). The rates of each fertilizer were set so that the same amount of nitrogen was supplied in each scenario. The use of ammonium sulfate in place of DAP resulted in a 12% increase in the total estimated acidification over the 4 years. Substituting with CAN resulted in an estimated acidification rate that was 15% lower than that when DAP was used and 24% lower than when ammonium sulfate was used. Naturally, factors such as price, availability, and efficacy will be the major determinants of the choice of fertilizer. However, we suggest that the cost of the acidifying effect of a fertilizer, in terms of the lime required to neutralize this acidification, should be factored into such considerations.

It is important to note that these estimated acidification rates are for the entire soil profile and do not attempt to apportion the acidification to soil layers.

TABLE 4 Estimated Acidification Rates for a Lupin–Wheat–Canola–Wheat Crop Sequence "Grown" on a Sandy Soil in the Medium Rainfall Zone (325–450 mm) of Western Australia[a]

Scenario	Crop, yield and N fertilizer application				Acidification rate	
	Lupin	Wheat	Canola	Wheat	kmol H$^+$ ha^{-1}	kmol H$^+$ ha^{-1} year^{-1}
1	1.9 t ha^{-1}	3 t ha^{-1}, 50 kg ha^{-1} urea, 50 kg ha^{-1} DAP	1.7 t ha^{-1}, 60 kg ha^{-1} urea, 60 kg ha^{-1} DAP	2.5 t ha^{-1}, 60 kg ha^{-1} urea, 60 kg ha^{-1} DAP	9.3	2.3
2	1.9 t ha^{-1}	3 t ha^{-1}, 50 kg ha^{-1} urea, 45 kg ha^{-1} amm. sulfate	1.7 t ha^{-1}, 60 kg ha^{-1} urea, 50 kg ha^{-1} amm. sulfate	2.5 t ha^{-1}, 60 kg ha^{-1} urea, 50 kg ha^{-1} amm. sulfate	10.4	2.6
3	1.9 t ha^{-1}	3 t ha^{-1}, 50 kg ha^{-1} urea, 35 kg ha^{-1} CAN	1.7 t ha^{-1}, 60 kg ha^{-1} urea, 40 kg ha^{-1} CAN	2.5 t ha^{-1}, 60 kg ha^{-1} urea, 40 kg ha^{-1} CAN	7.9	2.0

[a] Rates were calculated using the Lime and Nutrient calculator for three fertilizer scenarios that supplied the same quantity of nitrogen.

Acidification due to the leaching of nitrate and acidifying fertilizers will tend to occur in the topsoil, where the nitrification process occurs. In contrast, acidification resulting from the removal of alkaline produce, due to imbalance of cation and anion uptake, will tend to acidify the soil deeper in the profile (see Chapter 3). This is particularly true for legume species [28,35,49].

3.2   Comparing Predicted and Measured Values

Acidification rates under agricultural production systems in Western Australia have been determined from soil surveys [27,28,35,41]. In these studies acidification rates were estimated on the basis of the difference in soil pH between cleared and uncleared sites, using the formula developed by Helyar and Porter [1]. We compared these results with estimates made using the calculator (Table 5).

In all cases the calculator gave results that were higher than those estimated from the soil surveys. The contributions to acidification from the removal of alkaline produce (C cycle) were similar between the two estimates; however, the contribution from N cycle components (nitrate leaching and acidifying fertilizers) were higher using the calculator, by a factor of 2 on loam soils and a factor of 5–10 on sands.

Measured rates of nitrate leaching under agricultural systems in Western Australia are far higher than those that were previously estimated by difference [42]. These measurements, which were determined on deep, sandy soils in a medium- to high-rainfall zone, are at the upper end of leaching rates in this environment. However, they indicate the potential for nitrate to be leached. In addi-

TABLE 5   Comparison of the Average Acidification Rates for Five Rotations Calculated from Soil Surveys [27,28,41] and Using the Lime and Nutrient Calculator[a]

		Soil survey			Calculator		
		N cycle	C cycle	Total	N cycle	C cycle	Total
Rotation[b]	Soil type						
LWLWLW	Yellow sand	0.22	0.2	0.42	1.8	0.2	2
PPPWPPPW	Yellow sand	−0.13	0.34	0.21	1.3	0.3	1.6
PPPPPWLWW	Sandy duplex	−0.18	0.33	0.15	1.4	0.3	1.7
WWWWWW	Loamy sand	0.34	0.01	0.35	0.54	0.06	0.6
PWPWPW	Loamy sand	0.08	0.33	0.41	0.4	0.4	0.8

[a] Rates are divided into nitrogen cycle (nitrate leaching and nitrogen fertilizer) and carbon cycle (product removal) components.
[b] L, lupin (*Lupinus angustifolius*); W, wheat (*Triticum aestivum*); P, annual pasture (subterranean clover-based, *Trifolium subterraneum*).

tion, they highlight the importance of the asynchrony between supply of nitrate from mineralization and demand for mineral nitrogen by plants, which is a feature of many annual production systems throughout the world.

Dolling and Porter [27] stated that "the acidification rate and mechanisms in this study can only be taken as a guide as there are many potential sources of error," particularly pH buffering capacity. Recent work by Tang and colleagues [50] has highlighted the range of values of pH buffering capacity that are obtained using different laboratory techniques. They found that acidification rates calculated using pH buffering capacity accounted for only 59 to 65% of those measured in a pot experiment. In addition, acidification rates estimated from soil surveys assume that the soil acidification in uncleared areas is negligible, whereas even these "natural" ecosystems usually acidify with time [1].

3.3 Planning for Sustainable Production

Calculations such as those used in the preceding examples are useful to provide an estimate of the rate of acidification of a particular crop sequence. This information is an important first step in determining what applications of lime are required to maintain productivity. However, these calculations cannot be used in isolation. Estimated acidification rates need to be considered in conjunction with the results of soil pH tests and the sensitivity to acidity of the species being grown in order to ascertain whether neutralizing agents need to be applied to raise, or merely to maintain, soil pH. In combination, these pieces of information will allow farmers to make better informed decisions regarding the applications of liming agents to their paddocks or fields.

Estimates of acidification rates based on the contributions of the major components are helpful in identifying which aspects of agricultural systems could be altered to reduce rates of acidification. For example, is it possible to use a less acidifying fertilizer? What changes can be made to the system of production to reduce the leaching of nitrate [43,51–61]? These questions are critical as we develop agricultural systems that are better suited to the vagaries of an environment and are able to progress toward sustainable production of essential food and fiber.

4 CONCLUSIONS

The method used in this chapter to calculate acidification rates can be applied to agricultural production systems anywhere in the world. Estimates are obtained for the four main causes of soil acidification; removal of alkaline produce, accumulation of soil organic matter, leaching of nitrate, and use of acidifying fertilizers, using local data.

The ash alkalinity of harvested produce can be measured in a laboratory or calculated from chemical analyses of the product in question. Similarly, estimates

of the accumulation of soil organic matter and the composition of residues can be used to estimate these "removals" from the system. The acidifying effect of nitrogen and sulfur compounds used in manufactured fertilizers is well documented, so this component can be determined for any fertilizer based on its formulation. The acidification resulting from the leaching of nitrate produced in situ is the most difficult component to estimate. However, estimates will be made more easily as more measurements of the leaching of nitrate are being made worldwide because of recognition of the need to better manage inputs to help to control effects such as acidification and the eutrophication of waterways.

ACKNOWLEDGMENTS

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6

Modeling Acidification Processes in Agricultural Systems

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1 INTRODUCTION

Soil acidity increasingly limits production in agricultural systems in many parts of the world. Whereas in some cases the acidity is naturally occurring, in many others agricultural practices have accelerated soil acidification. A range of management practices has been proposed to control and ameliorate soil acidification. Liming has undoubtedly received most attention, but other options that have been suggested include the application of alternative ameliorants as well as modification of the production system through changes in crops grown, fertilizer, or residue management (see Chapters 12 and 13). Laboratory tests and field trials have assessed the effectiveness of many of these practices in increasing pH and reducing aluminum activity. Results have, however, often been variable. This is probably due to interactions with other processes operating in the system as well as the influence of weather and soil variability. Simulation models can be used to address these issues by integrating and extrapolating experimental observations. In this chapter we describe how incorporation of a proton budget framework into two models of agricultural systems provides us with tools to analyze soil acidification as a function of soil, climate, and agricultural management.

2 SOIL ACIDIFICATION: RELEVANT CONCEPTS

The processes involved in soil acidification have been described by, among others, van Breemen et al. [1], de Vries and Breeuwsma [2], Binkley and Richter [3], Helyar and Porter [4], and also by Bolan and Hedley (Chapter 2). As outlined by these authors, the various processes can be grouped according to the element cycle to which they belong. Table 1, for example, lists the main proton-producing and proton-consuming processes of the nitrogen cycle. The processes can also be presented in the form of diagrams [1–5]. Figure 1 is an example of such a diagram for the nitrogen cycle. From this, it was realized that in order to calculate the proton budget for processes associated with the nitrogen cycle, one needs only to keep track of changes in nitrate and ammonium. A reaction causing an increase in ammonium always leads to consumption of protons, whereas a decrease in ammonium leads to production of protons. The opposite happens for increases and decreases in nitrate. For example, mineralization of organic matter consumes one proton for every ammonium ion produced (reaction 2a), and nitrification leads to the production of two protons for every ammonium ion converted to nitrate (reaction 3). Similar diagrams can be drawn for the other element cycles. In these cycles, too, it is often necessary only to keep track of a few compounds.

The finding that only a few compounds need to be tracked led Helyar and Porter [4] to develop a proton budget framework based on three product pools: reference state, alkaline, and acid products (Fig. 2). In this framework, additions, losses, and accumulation of compounds in the alkaline or acid pools are associ-

TABLE 1 Selected Reactions of Proton-Producing and Proton-Consuming Processes in the Nitrogen Cycle

Process left to right[a]				Process right to left
(1) Urea hydrolysis	$(NH_2)_2CO + H_2O + 2H^+$	$\rightarrow$	$2NH_4^+ + CO_2$	
(2a) Mineralization of organic N	$RNH_2 + H_2O + H^+$	$\leftrightarrow$	$ROH + NH_4^+$	NH_4^+ immobilization (2b)
(3) Nitrification	$NH_4^+ + 2O_2$	$\rightarrow$	$NO_3^- + 2H^+ + H_2O$	
(4) Denitrification	$5CH_2O + 4NO_3^- + 4H^+$	$\rightarrow$	$2N_2 + 5CO_2 + 7H_2O$	
(5) NO_3^- immobilization	$ROH + NO_3^- + H^+ + 2CH_2O$	$\rightarrow$	$RNH_2 + 2CO_2 + 2H_2O$	
(6) NH_3 volatilization	NH_4^+	$\rightarrow$	$NH_3 + H^+$	
(7) Uptake of NH_4^+	$ROH(plant) + NH_4^+$	$\rightarrow$	$RNH_2(plant) + H_2O + H^+$	
(8) Uptake of NO_3^-	$ROH(plant) + NO_3^- + H^+ + 2CH_2O$	$\rightarrow$	$RNH_2(plant) + 2CO_2 + 2H_2O$	

[a] Numbers refer to the schematic presentation in Fig. 1
Adapted from: Ref. 2.
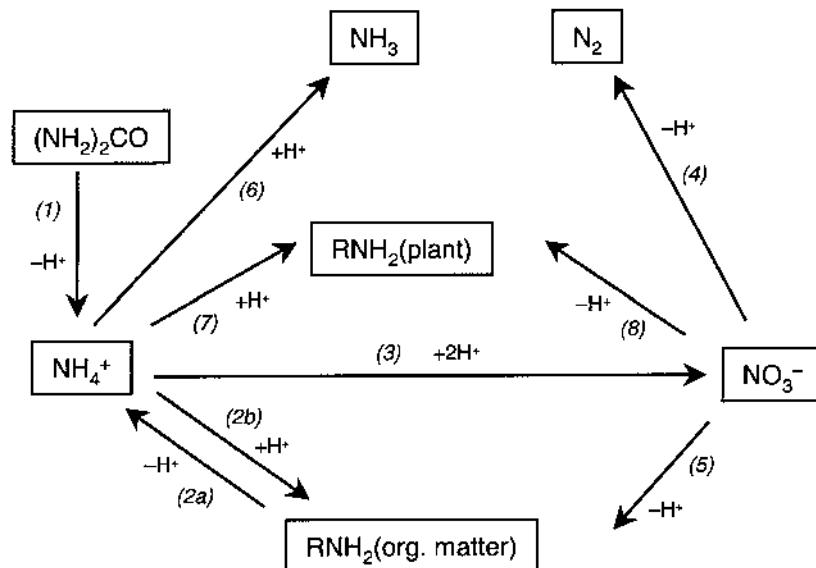
FIGURE 1 Schematic presentation of the proton-producing ($+H^+$) and proton-consuming ($-H^+$) reactions in the nitrogen cycle; numbers refer to the reactions listed in Table 1.
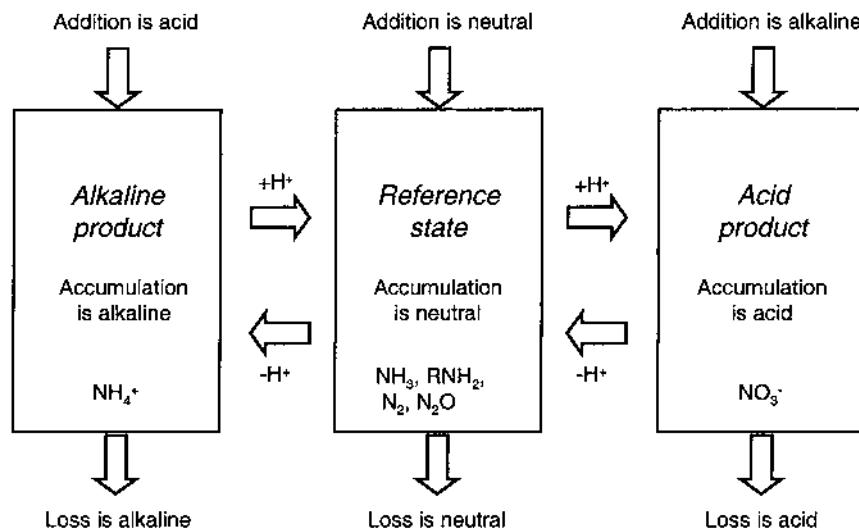
FIGURE 2 Three product pools for determining acid production by the nitrogen cycle. (Adapted from Ref. 4.)

ated with the net production or consumption of protons. Additions, losses, and accumulation of products in the reference state are considered neutral, as are transformations between products within this pool. For practical purposes the reference state is defined so that the measurements required to establish the proton budget are as simple and practical as possible. For the nitrogen cycle, for example, only measurements of nitrate and ammonium fluxes and accumulation are required to calculate the net effects on acidification of all the reactions in Fig. 1. Ammonium is considered an alkaline product, meaning that its addition is counted as proton producing (acid) and its accumulation and its loss are counted as proton consuming (alkaline). Nitrate, on the other hand, is considered an acid product, with addition being equivalent to consuming protons (alkaline) and accumulation and loss equivalent to producing protons (acid). Note that the additions and losses do not themselves involve production or consumption of protons, but the net effect of these processes relative to the reference state does. For example, loss of nitrate through leaching is not acidifying in itself but only following mineralization and nitrification of organic nitrogen: mineralization to ammonium consumes one proton, nitrification produces two protons, so that the net effect is a production of one proton for every nitrate ion accumulated or leached.

Similar pools were defined for the carbon cycle, leading to a net acid addition equation:

$$
\begin{aligned}
\text{Net acid addition} ={}& \text{(carbon cycle effects)} \\
& + \text{(nitrogen cycle effects)} \\
& - \text{(addition of other alkalis)} \\
& + \text{(net addition of acids)} \quad\quad\quad\quad (1) \\
={}& (OA_{ac} + OA_{ex} - OA_{ad} + HCO_{3ac} + HCO_{3ex} - HCO_{3ad}) \\
& + (NH_{4ad} - NO_{3ad} - NH_{4ac} + NO_{3ac} - NH_{4ex} + NO_{3ex}) \\
& - (L_{ad}) \\
& + (H_{ad}) - (H_{ex})
\end{aligned}
$$

where the units of net acid addition are mol H^+ ha^{-1} $period^{-1}$ and ac stands for accumulation, ex for loss, and ad for addition. OA represents the organic anions in organic matter, residues, and removed plant products; HCO_3 represents the bicarbonate products in solution; and L represents lime or other alkali additions. Helyar and Porter [4] give a detailed description of the various terms and how they are measured or estimated.

Because the Helyar and Porter model considers acid production and consumption relative to the reference state, Eq. (1) needs to be used with care. For example, addition of an ammonium fertilizer (NH_{4ad}) is considered acid although it does not lead to acidification if it remains as ammonium in the soil. Ammonium accumulation (NH_{4ac}) is calculated as alkaline, so the two terms balance each

other out. Similarly, nitrate leaching (NO_{3ex}) is calculated as acid but in itself does not lead to acidification as it leads to a reduction in accumulated nitrate (NO_{3ac}), a term that is accounted as alkaline. Denitrification, an alkaline process whereby nitrogen is lost as one of the gases N_2, N_2O, or NO, which are all in the reference state, is represented as a reduction in accumulated nitrate (NO_{3ac}).

Not all proton-producing and proton-consuming reactions are represented in Eq. (1). In particular, those relating to buffering of soil pH (cation exchange, weathering) are not included. These are the inorganic reactions that occur in the soil in response to the addition of acids or alkalis. A full budget is, therefore, not calculated. Instead, the Helyar and Porter framework combines Eq. (1) with an equation describing the change in pH over a given period as a function of net acid addition during that period and the soil pH buffer capacity (pHBC):

$$\text{pH change} = \frac{\text{net acid addition}}{\text{pHBC} \times \text{W}} \tag{2}$$

where the pH buffer capacity is defined as mol H^+ kg^{-1} (pH unit)$^{-1}$, and W is the weight of the component of the ecosystem to which the pH buffer capacity applies (kg ha^{-1}).

The Helyar and Porter framework has been used in several Australian studies to determine the main factors causing accelerated acidification in soils under agriculture. Within the carbon cycle, these were found to be accumulation of organic anions in soil organic matter and removal of organic anions in products or their transfer in animal excreta to stock camps [4,6–11]. Within the nitrogen cycle, the single most acidifying cause was the leaching of nitrate following nitrification of ammonium, which was either applied as fertilizer or mineralized from organic nitrogen [12,13].

In most studies the model has been used in a retrospective mode because an estimate of the nitrate leaching term (NO_{3ex}) was unavailable. Long-term data on the change in soil pH were obtained from historical records or samples (e.g., [11]) or derived from fenceline comparisons (e.g., [12–14]) and combined with pH buffer capacity data to calculate the net acid addition over the period studied. By equating Eqs. (1) and (2) when both were arranged to estimate net acid addition, the nitrate leaching term was obtained by difference. Other terms in Eq. (1) were either calculated from measurements or from historical records or were assumed to be negligible (HCO_{3ac}, NH_{4ac}, NO_{3ac}, NH_{4ex}). This approach effectively assumes that all acidification that cannot be accounted for by other processes is due to nitrification of ammonium followed by nitrate leaching with a strong alkali cation [15]. Unfortunately, this can lead to large uncertainties or even erroneous results. Dolling and Porter [8] and Dolling et al. [9], for example, arrived at negative values (suggesting an alkaline effect) for the NO_{3ex} term, which is supposed to be acidifying. It indicates that the error in their calculations was at least of the same magnitude as the nitrate leaching term. Uncertainty in the nitrate leaching

term is probably also why estimates of the relative contributions of carbon and nitrogen cycles to acidification have been highly variable (e.g., [6,7,16]).

The pH buffer capacity can be an important source of error in the application of the Helyar and Porter framework. Changes in pH buffer capacity over time are usually ignored due to lack of data. This can lead to under- or overpredictions of proton production, especially in situations where the levels of organic matter changed dramatically over the period of study. In addition, slow buffering reactions such as dissolution of aluminosilicate minerals are often not included when the pH buffer capacity is measured using a short period of reaction. This leads to underestimation of proton production by Eq. (2) [14]. Furthermore, Porter et al. [15] emphasize that organic anion accumulation in soil organic matter and organic anion export to stock camps are calculated using conversion factors of questionable accuracy. All these factors increase the uncertainty in the nitrate leaching term when the model is used in a retrospective mode with nitrate leaching loss being estimated from the unaccounted component of acid addition. It is noted that Moody and Aitken [12] point out that processes such as denitrification, volatilization, and leaching of organic acids with subsequent deprotonation are ignored, but this is not a problem because effects on the proton budget of losses of carbon or nitrogen in the reference state are taken into account by the accounting system.

Despite these limitations, the framework has been useful for discerning the main causes of soil acidification in various agricultural systems and for identifying possible strategies for reducing soil acidification. Moody and Aitken [12], for example, performed sample calculations to analyze the potential effect of changes in management practices under bananas, and Ridley et al. [6] made suggestions for improved pasture management based on an analysis of carbon cycle acidification. Similarly, application of the framework to two *Leucaena*-based pastures in different locations (humid subtropical environment vs. semiarid tropics) has highlighted the effect of climate on some of the acid balance terms ([11], A.D. Noble and R.J. Jones, CSIRO Land and Water and CSIRO Tropical Agriculture, Townsville, personal communication, 1997).

Two studies applied the Helyar and Porter model in prospective mode. Ridley et al. [16] and Poss et al. [17] calculated nitrate leaching by combining drainage data with measured nitrate concentrations in deep soil water or drainage water. While allowing a direct assessment of the effect of nitrate leaching on acidification, the proton budget calculations are in this case restricted to the limited length of such detailed field experiments. Calculated pH changes could, therefore, not be verified as they were of the same order as seasonal variability in soil pH [16].

Several studies have shown that the rate of acidification or pH change within the soil profile is not uniform with depth (e.g., [17–20]). Similarly, the pH buffer capacity is not constant with depth (e.g., [14,21]). In the application of the Helyar and Porter framework, Eq. (2) is therefore applied to the individual soil sampling depth intervals, and a total acid increment for the profile is obtained by

summing these acid inputs. Despite recognition of the differential rate of acidification within the profile, however, most studies persist in applying Eq. (1) of the Helyar and Porter framework to the profile as a whole. Especially in cases where acidification occurs in the topsoil while alkalinization occurs in the subsoil or vice versa, this bulk assessment could fail to recognize the importance of the various processes contributing to development of pH profiles. When Poss et al. [17] applied the Helyar and Porter framework separately to topsoil and subsoil, they found little acidification of the profile as a whole, corresponding to little nitrate leaching out of the root zone. There was, however, significant movement of nitrate within the profile, resulting in acidification of topsoil due to nitrification there and alkalinization of subsoil following uptake of nitrate by plant roots. An analysis of acidification at the soil layer level is therefore useful and might help identify or improve management strategies aimed at ameliorating topsoil or subsoil acidification.

In this context, the transport of acidity and alkalinity within the profile is important as well. An earlier multilayer implementation of the Helyar and Porter framework, the SPAM model (Soil Profile Acidification Model [22,23]), partly addressed this issue. It used a net acidification rate of the profile as a whole derived from Eq. 2 and distributed this acidity on the basis of movement of alkalis and acids within the profile and ion intake balances for the roots in each layer. Nitrate absorption patterns were obtained by fitting against actual pH data. Although retrospective, the model proved useful in the analysis of profile acidity development.

The uncertainty in nitrate leaching, the transport of acidity within the profile, and the need to analyze soil layers separately are issues that can all be addressed if the Helyar and Porter framework is combined with a model that simulates the underlying carbon and nitrogen cycle processes (including nitrate leaching) and ion uptake and excretion in each layer. Two Australian agricultural systems models, GRAZPLAN [24] and APSIM (Agricultural Production Systems Simulator [25]), are particularly suited to linkage with the proton budget calculations. These models predict, at the soil layer level, all the major transformations and fluxes of carbon and nitrogen that contribute to soil acidification. For example, in APSIM the soil residue module simulates decomposition of residues and the effect of various tillage practices, and the soil nitrogen module describes urea hydrolysis, mineralization, immobilization, nitrification, and denitrification [26]. Uptake of nitrogen is part of the crop modules, and transport and leaching of nitrogen are simulated by the water balance modules Soilwat [26] or SWIM (Soil Water Infiltration Movement [27]). Because both GRAZPLAN and APSIM predict nitrate leaching, development of a soil acidification module in these agricultural systems models allows not only quantification of soil acidification but also, in contrast to the retrospective use of the Helyar and Porter framework, prediction of changes in pH.

Another advantage of implementing the proton balance calculations within these agricultural systems models is that it provides the ability to conduct

simulations using long-term weather data sets. These simulations can be used to explore experimental outcomes or to predict the impacts of weather and management on soil pH change (so-called *what-if* scenarios). Extrapolation of experimental results to other soil types or weather conditions is also possible. Modeling thus provides opportunities for analyzing the effect of different management options aimed at reducing or ameliorating soil acidification.

The Helyar and Porter proton budget calculations have been implemented in both APSIM and GRAZPLAN. These developments (APSIM-SoilpH and the GRAZPLAN soil acidity model) have been largely independent because of the history and different focus of the models: GRAZPLAN deals with grazing enterprises, whereas APSIM is mainly concerned with cropping systems. In this chapter we describe how the proton budget equations have been implemented in the two models, discuss some of the difficulties of capturing complex and interacting processes in models, and give illustrations of model usage. Both acidification models are currently undergoing testing. Results presented here are, therefore, preliminary. Nevertheless, we hope that the examples give an idea of the opportunities that are provided by modeling of acidification processes as well as presenting an understanding of some critical aspects such as parameterization requirements and model limitations.

In the next section we first provide relevant background details of the "parent" models GRAZPLAN and APSIM before describing their acidification modules. These descriptions are followed by examples from both models, and we conclude the chapter with some remarks on opportunities and limitations of model usage and plans for further developments.

3   GRAZPLAN AND APSIM: TWO AGRICULTURAL SYSTEMS MODELS

Models are powerful tools in many fields of research, development, and management. Two models that in recent years have contributed to Australian agricultural systems management and research are GRAZPLAN and APSIM. GRAZPLAN is a suite of decision support tools aimed at helping farmers manage grazing enterprises. It is being developed by scientists at CSIRO Plant Industry. APSIM was originally designed as a tool for systems research, allowing a combination of different soil, crop, and pasture models to simulate soil and crop management dynamically using conditional rules. It has, however, also been used in extension activities to assist farmers in managing crops and croplands. APSIM is being developed by the Agricultural Production Systems Research Unit (APSRU), a collaboration between the CSIRO Divisions of Sustainable Ecosystems (CSE) and Land and Water (CLW) and the Queensland Department of Primary Industries (QPI) and Natural Resources and Mines (DNRM).

3.1 GRAZPLAN*

Publicly available decision support tools included in the GRAZPLAN suite are MetAccess for analysis of weather data [24], LambAlive for lamb mortality [24], GrazFeed for feeding tactics [28], and GrassGro [29] for pasture and animal production. Embedded in these decision support tools are dynamic simulation models that describe certain aspects of the system, e.g., pasture growth, soil moisture, and animal biology. The most recent development within GRAZPLAN is NutriAce (Fig. 3). It is available as a prototype and capable of simulating the cycling of carbon, nitrogen, phosphorus, and sulfur in the grazed pasture systems of temperate Australia. The soil acidity model is part of this development.

Simulations in NutriAce are run on a daily time step, with the user specifying initial conditions and parameter values that describe the specific location, the pasture, and the animal enterprise being simulated. NutriAce uses weather data held in MetAccess weather files [24]. Pasture and sheep or beef enterprises are simulated using the pasture and animal models from the GrassGro decision sup-

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* For more information visit the web site http://www.hzn.com.au/grazplan.htm.
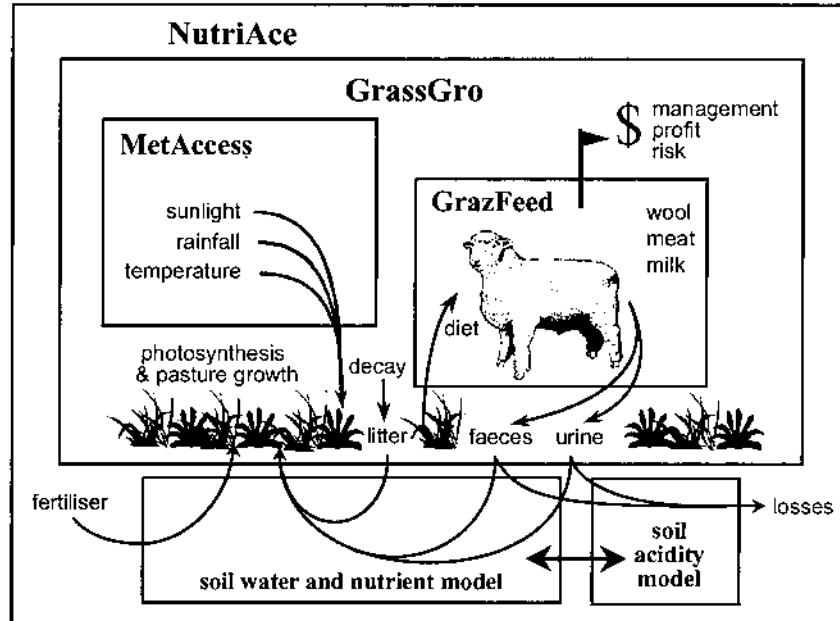
FIGURE 3 Structure of NutriAce.

port tool [28,29]. These models have been extended to include cycling of nitrogen, phosphorus, and sulfur. Pasture may comprise a mixture of plant species. This is particularly important because nitrogen inputs to many Australian grazing systems are mainly through nitrogen fixation by pasture legumes. The soil water model is also an adaptation of that used in GrassGro. The soil nutrient component of NutriAce is a further development of the soil nutrient cycling component of the McCaskill–Blair model [30–32].

The GRAZPLAN decision support tools MetAccess, GrassGro, and Grazfeed are already successfully used by consultants, rural advisers, and graziers in a diverse range of activities, from drought feeding strategies and optimizing lambing time to fodder reserve policies and decisions on various grazing management options [33–35]. NutriAce was designed to help graziers develop longer term fertilizer strategies. Testing of the prototype version of NutriAce has demonstrated that there is a range of production issues to which the model can be applied and that plausible simulations of pasture systems can be made.

Although developed as decision support tools for farmers and their advisors, the different components of GRAZPLAN have also been used in systems research. Donnelly et al. [36], for example, used GrassGro to evaluate criteria for the definition of exceptional drought, Cayley et al. [37] used it to compare spring and autumn lambing options, and Hill et al. [38] used GRAZPLAN in combination with satellite data to describe spatial variability in pasture growth at a farm scale. An example of model use in economic analysis is that of Scott and Cacho [39], who used production figures from GrassGro simulations to underpin a long-term investment analysis of fertilizer policies.

3.2 APSIM*

The APSIM framework has a modular structure in which crops and major soil processes are dealt with in separate modules (Fig. 4). These modules can be plugged into and out of the system as required. Thus, it allows the choice of a configuration of modules that best reflects the system to be simulated. Another feature of the model is that the soil provides a central focus; crops, seasons, and managers come and go, finding the soil in one state and leaving it in another [25]. Currently there are 25 crop or pasture modules, 10 soil and related modules, and a number of program management and control modules. Communication is via the central engine, with all active modules called once a day in a user-specified order.

The user has a choice of two water balance modules: SoilWat, a tipping bucket module, or SWIM, which is based on a numerical solution of the Richards equation. Dynamics of soil organic matter are dealt with by the SoilN module and decomposition of surface residues in the Residue module. Multiple crop modules

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* For more information, visit the web site: http://apsim-help.tag.csiro.au/
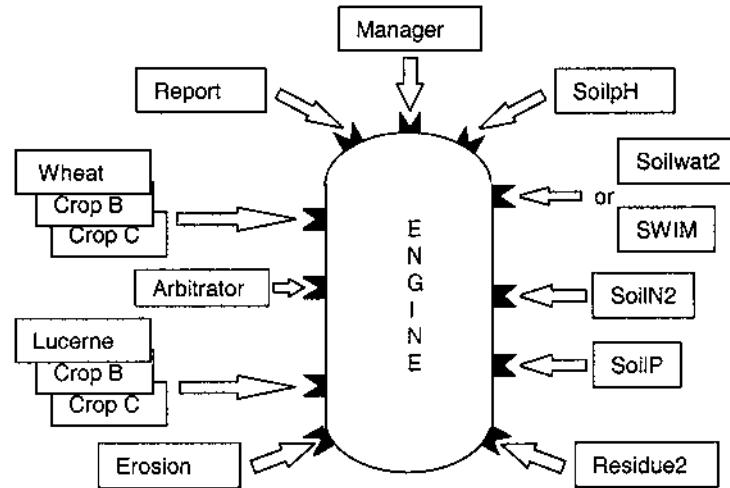
FIGURE 4 The modular structure of APSIM that allows modules to be pulled out or plugged in. (Adapted from Ref. 25.)

can be active at any time, with APSIM handling intercropping issues such as competition for light, water, and nitrogen. A powerful module in the simulation of many scenarios is the Manager module. It provides a user-defined, flexible, and rule-based management system that permits a simulation to mimic realistically both natural and interventionist actions within the system (e.g., to sow on a specified criterion based on rainfall and soil water). Field operations such as sowing, irrigation, or tillage are executed in response to calls to the operations module or activated by statements in the manager logic.

APSIM's performance in relation to specific modules has been reported in a number of studies (e.g., Wheat [40]; Lucerne [41]; Sugar [42]; SoilWat, SoilN, and Residue [26]). Various APSIM configurations have been tested against experimental data and subsequently used with historical weather records to analyze temporal variability and explore soil and crop management scenarios. For example, a configuration including Wheat and SoilWat was used by Asseng et al. [43] to simulate yield, deep drainage, and nitrate leaching for a deep sand in Western Australia and study the effect of split applications of nitrogen fertilizer. Management of nitrogen fertilizer was also the focus of studies by Keating et al. [44] and Verburg et al. [45], who looked at the impact of irrigation management and soil fertility on nitrate leaching under sugarcane using a configuration based on SWIM and Sugarcane. Impact of management of legume–cereal systems on productivity and soil fertility was the focus of studies by Carberry et al. (Stylosanthes, Sorghum [46]) and Probert et al. (Chickpea, Wheat [47]). Scenario analysis based

on historical weather records was also carried out by Keating and Meinke [48], who used APSIM with Wheat and Sorghum and historical weather records to assess exceptional drought in grain-producing areas of northeast Australia.

4 IMPLEMENTATION OF THE HELYAR–PORTER PROTON BUDGET FRAMEWORK

The proton budget of Eq. (1) can in principle be applied to a system at any scale. Implementation of the Helyar–Porter framework in the two agricultural systems models implies a change from the whole profile approach taken by most experimental studies to that of a multilayered soil system. The corresponding changes in system boundaries require modification of the definitions of some of the proton budget terms. These modifications and other aspects, such as the impact of a shift from an annual to a daily time step, are discussed in this section.

4.1 System Boundaries and Implications for Proton Budget Terms

In the "original" application of the Helyar and Porter framework to a whole soil profile, the plants (dead and alive) were included in the system. Effectively, the system was defined by the boundaries of the farm field and the bottom of the root zone. Additions and exports [ad and ex terms in Eq. (1)] occurred at these boundaries (see Fig. 5a). For example, OA_{ex} represented the alkalinity in exported products, NO_{3ex} the nitrate leached below the root zone, and NH_{4ad} any ammonium fertilizer added.

This definition of the system allowed certain simplifications to be made. Excretion of protons or bicarbonate ions at the surface of roots due to imbalances in ion uptake ("root excretion" [49]; see also Chapter 3) could be ignored as it was inside the system and because the return of organic anions in residues was not taken into account either. Only the proportion that matched alkalinity in exported products was taken into account (acidifying effect of OA_{ex} term). Uptake of nitrate and ammonium was not included in the NO_{3ex} and NH_{4ex} terms, as it too was defined to occur within the system. This exclusion of uptake was possible because the corresponding excretion of protons and bicarbonate ions was not taken into account.

Application of the Helyar and Porter framework to multilayered soil systems does not allow these simplifications, as the amount of proton/bicarbonate excretion varies with depth. In addition, its location is different from that of the alkalinity that is returned in the form of organic anions in residues. The additions and exports now happen at the soil–plant interface and at the boundaries between layers (Fig. 5b). This also means that transport within the profile must be taken into account: exports from one layer are additions to the next layer. Transport of aluminum, which could be ignored in the whole profile treatment, is now an important factor in modeling transport of acidity.
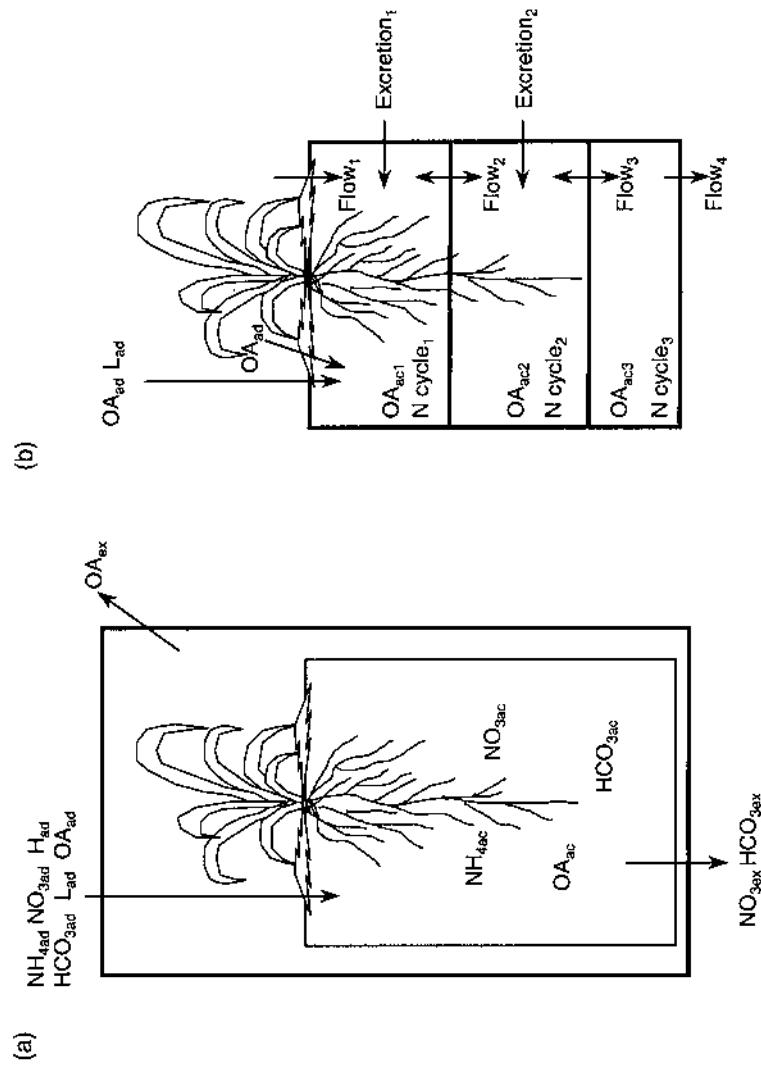
FIGURE 5 System boundaries (thick boxes) and proton budget terms in (a) the "original" application of the Helyar and Porter framework to a whole soil profile and (b) the adapted model implementation for a multilayered soil system. See text for an explanation of abbreviations.

The implementation of the Helyar and Porter framework in multilayered soil systems, therefore, requires the following modifications:

1. additional term for root excretion,
2. inclusion of returned residues in the OA_{ad} term,
3. calculation of transport of acidity (including aluminium) between layers.

As a consequence, Eq. (1) has a slightly different form in the implementations in GRAZPLAN and APSIM:

$$
\begin{aligned}
\text{Net acid addition} = {}& \text{nitrogen cycle effects} \\
& + \text{net root excretion} \\
& + \text{net effect of reactions involving organic anions} \\
& + \text{other element cycle effects} \\
& - \text{lime dissolution} \\
& + \text{net mass flow of acidity}
\end{aligned}
\tag{3}
$$

The bicarbonate fluxes in the system [HCO_3 terms in Eq. (1)] are included in the net mass flow of acidity. The net effect of reactions involving organic anions refers to the release of alkalinity or acidity from returned plant residues and animal excreta or urine, due to association or dissociation of weak acid groups, the oxidation of organic anions, and the effects of dissociation of weak acid groups following humification of uncharged organic pools. In the "original" Helyar and Porter framework [Eq. (1)] these processes were captured by the OA_{ad} and OA_{ac} terms. The various processes and their parameters are discussed in more detail in the following.

4.2 Proton Production Due to Nitrogen Transformations

The net proton production or consumption due to processes of the nitrogen cycle is calculated in both models according to

$$
\text{Nitrogen cycle effects} = \text{net transformation } NO_3 - \text{net transformation } NH_4 \tag{4}
$$

where net transformation NO_3 is the net production of nitrate due to all transformation processes affecting the creation or consumption of nitrate [i.e., reactions (3), (4), and (5) in Fig. 1] and net transformation NH_4 is the sum of all transformation processes affecting the creation and consumption of ammonium [i.e., reactions (1), (2), (3), and (6) in Fig. 1]. This definition of the nitrogen cycle contribution differs from that given by Helyar and Porter [4] [Eq. (1)] as the addition and export terms of ammonium and nitrate are not included, whereas those of denitrification and ammonia volatilization are. Plant uptake of nitrate and ammonium [reactions (7) and (8) in Fig. 1] is also not included because the net effects of up-

take of all ions are accounted for in the net root excretion term. Only the protons associated with transformations between the three boxes in Fig. 2 are included, as these are the chemical processes producing or consuming protons (Table 1). This approach of focusing on the actual proton-producing and proton-consuming processes has an advantage over the approach in Eq. (1) because it emphasizes that it is, for instance, not nitrate leaching per se that causes acidification but protons generated during nitrification. Leaching essentially separates nitrate from the protons, ensuring that further transformations will not consume them.

4.3   Net Root Excretion

Root excretion (protons or bicarbonate ions) occurs so that the net charge balance due to uptake of cations (e.g., NH_4, Na, Mg, Ca, and K) and anions (e.g., NO_3, Cl, SO_4, and H_2PO_4) is zero. The effect of absorption of trace elements is usually negligible but may be important in some situations (e.g., for high Mn uptake). The magnitude of acid or alkali excretion from roots is equal to the overall balance of cation to anion uptake. Inside the plant most of the inorganic nitrogen and some of the sulfur is reduced or oxidized into organic compounds. The remaining excess of cations or anions (generally cation excess) is compensated for by organic anions ($RCOO^-$). As decomposition of the plant material causes these organic anions to consume protons, they represent an amount of alkalinity that has been withdrawn from the soil system. Subsequently, this alkalinity may be wholly or partly exported as products and animal excreta or returned as plant residues. The magnitude of the acid excretion from roots due to the uptake of nonmetabolized cations less nonmetabolized anions is equal to the sum of the exported and returned alkalinity. The acid excretion to balance nitrate and ammonium uptake is equal to the difference between these two uptake terms ($NH_4 - NO_3$). Where the outcome is excretion of bicarbonate ions, the models assume absorption of protons instead, to avoid calculation of the equilibrium between bicarbonate and carbon dioxide in the soil air.

Nitrate and ammonium uptake are simulated dynamically by the two models so that the corresponding absorption or excretion of protons is made to match time and location of uptake. As not all of the other ions are simulated explicitly by the models (GRAZPLAN handles phosphorus and sulfur, APSIM only phosphorus), the proton excretion matching the excess cation uptake needs to be estimated in other ways. The two models handle this slightly differently. It should be noted that both approaches are simplifications of reality because of the limited experimental information on timing and location of ion uptake.

In the GRAZPLAN soil acidity model, the proton excretion due to excess nonmetabolized cation uptake is estimated as the product of the excess cation contents of the shoot and root material and the total net primary productivities of these components. Currently, the values for excess cation content of plant shoots and roots are assumed to be constant characteristics of each plant species. Proton ex-

cretion is distributed between the soil layers in proportion to root mass, but the proportions are weighted according to a decreasing function of layer pH to take account of the concentration gradient against which the root proton pumps must operate [50].

In APSIM, the crops have several aboveground components that have different fates (e.g., harvested products, returned residues) and often different excess cation contents. Dynamic simulation of the corresponding proton excretion during plant development is complicated. For example, in the case of cereals the nutrients that end up in the grain may have been translocated late in crop growth from stem and leaves into grain [51,52]. Hence, the protons that ultimately "match" the alkalinity in the grain may have been excreted before grain development starts. Leaf fall during the season causes similar problems, as it is not reflected in dry matter weights and excess cation contents measured at harvest.

APSIM-SoilpH, therefore, deals with proton excretion due to excess nonmetabolized cation uptake on an event basis. Examples of events are harvest, crop cuts (e.g., lucerne), crop burns (e.g., sugarcane), and leaf fall. Upon occurrence of an event, the excess cation contents of the relevant plant components (e.g., only leaves in case of leaf fall, all aboveground components in case of harvest) are calculated and summed to determine the total proton excretion due to excess nonmetabolized cation uptake since the last event. The disadvantage of this approach is a mismatch in timing—proton excretion due to excess nonmetabolized cation uptake occurs only at predefined events rather than continuously throughout the season. It was deemed, however, that this was necessary to avoid artificial generation of acidity or alkalinity that may occur when calculating daily proton excretion using an "average" excess cation content based on estimated proportions of returned and exported components. Although the APSIM-SoilpH structure includes a component for excess cations in roots, it is not currently considered in the calculations. Root alkalinity or ion concentration data are scarce. This term is, therefore, ignored on the assumption that alkalinity of roots is released in the same layer where protons were excreted.

In calculating the amount of protons excreted in response to excess nonmetabolized cation over nonmetabolized anion uptake (i.e., excluding nitrate and ammonium), APSIM-SoilpH considers the individual ion concentrations rather than the excess cation content. It does so to allow specified profiles for uptake of each ion. Ions are absorbed in proportion to the root length in a layer unless there is reason to believe that the availability of the ion varies significantly between layers. For example, the availability of phosphorus is usually biased heavily to topsoil layers [53,54]. By comparison, the availability of calcium, magnesium, and potassium is often more evenly distributed down the profile [55], so an absorption pattern more closely aligned to root length is appropriate. Where, however, the availability of these cations is known to vary significantly with depth, this can be expressed in the model through the use of ion availability indices.

4.4   Fate of Organic Anions

The fate of organic anions accumulated in the plants varies. Some are returned to the system with plant residues. As discussed previously for crops in APSIM, part of the organic anions may also be exported with products such as cereal grain, sugarcane stem, and pasture hay. In grazed pastures, animals may consume organic anions as part of the feed intake. These organic anions can be returned to the system as feces or urine or be exported via product removal (meat, milk, and wool).

The GRAZPLAN soil acidity model simulates the uptake and excretion by livestock of nutrients and organic anions. Uptake of organic anions follows from the prediction of the intake of energy and protein. The model allows selective grazing and substitution by supplementary feeds and calculates use of the diet for both maintenance and production (e.g., meat, wool, pregnancy, and lactation [28]). An organic anion mass balance is computed for the animals, based on the simulated organic anion contents of their intake and constant organic anion contents for production of wool, fleece-free body weight, and feces [56], with the remaining organic anions excreted in urine. The export of organic anions from the system via product removal (meat, milk, and wool) is estimated by accumulation of the amounts in each day's animal production.

On a grazed paddock the excretion of feces and urine is not evenly distributed. Sheep camp areas receive large proportions of excreta at the expense of the rest of the paddock [57]. In addition, urine is excreted in patches of locally high nutrient input [58]. In the GRAZPLAN soil acidity model, losses of both nutrients and organic anions due to transfer into camp areas are estimated as a constant proportion of the total excretion. Inorganic nutrient dynamics under urine patches are modeled separately; urine excretion, apart from that in the camps, is assumed to be spread over a small proportion of the field, affecting the rate of uptake by plants and the leaching of urine-derived nitrate.

4.5   Reactions Involving Organic Anions

Oxidation of the organic anions that are returned to the soil consumes protons and hence delivers alkalinity to the system. In addition, association or dissociation of weak acid groups in returned plant residues, animal excreta, and soil organic matter leads to consumption or production of acidity. The effects of these reactions on the proton budget are handled slightly differently by the two models.

In APSIM, return of crop residues is simulated by the crop modules and occurs at events such as harvest and with leaf fall. The organic anion content of the returned material, expressed as (ash) alkalinity, is mixed with that of any residues already on the soil surface. The subsequent fate of the residues is simulated by the residue module. Residues may be burned, incorporated to a certain depth in the soil to become part of the fresh organic matter pool upon tillage, or left to decompose on the surface in response to factors such as moisture, C/N ratio, and temperature.

When surface residues are left to decompose on the surface, the release of alkalinity follows this (slow) decomposition and alkalinity is released upon transfer of carbon and nitrogen from the surface residues to the soil organic (microbial and humus) pools. In the case of residue incorporation, alkalinity is assumed to be released instantaneously. Pot experiments have suggested that, in reality, release of alkalinity due to decomposition from the fresh organic matter pool may take a few days or weeks [59–61], so that there may be a small timing error here.

In APSIM, burning of residues releases alkalinity instantaneously in the surface 5 cm, unless immediately followed by incorporation to a specified depth. In this case, instantaneous release is probably close to reality. Allowance is made for a user-determined loss factor for material blown away in the fire.

APSIM-SoilpH does not keep track of organic anions in the soil. Once surface residues are burned, incorporated, or decomposed into soil organic matter pools, the alkalinity associated with their organic anions is released. Any accumulation or depletion of organic anions in the soil, due to accumulation or depletion of carbon or association/dissociation reactions, is instead estimated from an empirical equation for the organic anion content of soil organic matter and changes in the soil organic matter content. This equation, adopted from Helyar and Porter [4], treats organic anions as Brønsted–Lowry alkalis and takes into account not only their net accumulation but also their change in association/dissociation due to changes in pH. The organic anion content is equated to the cation exchange capacity of the soil organic matter, which is given by

$$\text{CEC(SOM)} = a(\text{pH} - b) \tag{5}$$

This relationship was derived [4] from measurements of whole soil CEC, clay, and organic matter contents of 60 Wisconsin soils at various pH values [62] and soil humic acid titration curve data presented by Kononova [63]. The parameter a varies between 0.07 and 0.83 $\text{mol}_c\ \text{kg}^{-1}$ soil organic matter, depending on the density of pH-dependent groups in the organic matter (usually higher in more decomposed material). The parameter b represents the pH for zero charge of the organic matter. Helyar and Porter [4] arrived at a value of 1.5 for b, based on the data in Helling et al. [62] and Kononova [63]. For organic-rich soils in New Zealand, De Klein et al. [64] derived a value of about 3. Both a and b are user-defined inputs to APSIM-SoilpH, to accommodate the comments by Porter et al. [15] and Poss et al. [17] that the a and b values suggested by Helyar and Porter [4] contain some uncertainty due to being quantified for only a narrow range of soils.

To determine the accumulation or depletion of organic anions, the pH-dependent organic anion content needs to be multiplied by the change in organic matter content. This is based on changes in the microbial and humus pools predicted by the soil nitrogen module and a factor between 1.7 and 1.9 (user defined) to convert organic carbon to organic matter [4]. Accumulation of organic anions

is equated to proton production in the proton budget [Eq. (3)], with depletion representing proton consumption.

The preceding approach of APSIM-SoilpH to handling reactions involving organic anions is similar to the original Helyar and Porter framework with its OA_{ad} and OA_{ac} terms. It is a simplification of reality. Due to the daily time step of the model, the approach causes some errors in the timing of alkalinity release, especially with incorporated residues. The errors are only temporary, however, lasting for periods of a couple of weeks to a cropping season at most, and would hence be acceptable for most model applications.

In contrast to APSIM-SoilpH, the GRAZPLAN soil acidity model does keep track of organic anions (or their proton equivalents) in the soil. In this model organic matter is contained in four organic matter pools (labile and resistant fresh organic matter, microbial biomass, and humus). The sizes of these pools are defined in terms of organic carbon (C). The organic anion contents of the pools are expressed as ratios of the proton equivalents to organic carbon (H/C ratios). Decomposition of the organic matter is tracked by the transfers of organic carbon between these pools. Three fates are identified for organic carbon: synthesis into microbial biomass, respiration as CO_2, or conversion into humus. Alkalinity associated with synthesized organic carbon is moved to the microbial biomass pool (as organic anions), while that associated with respired carbon is released and taken into account in the proton budget [Eq. (3)]. The conversion to humus takes into account the H/C ratios of the newly formed humus and that of the existing humus pool. The latter is assumed to be dependent on soil pH in a similar way as expressed by Eq. (5). In case of an imbalance between the two ratios, protons are consumed or produced, a process that is reflected in the proton budget [Eq. (3)]. The model uses an a value [Eq. (5)] appropriate for humic acids (0.83 mol_c kg^{-1}) and an OM/C ratio of 1.72 [65].

Upon incorporation of plant residues (physical movement due to mesofauna, trampling, and pugging), only a proportion of their alkalinity is released immediately:

$$\text{Alkalinity released immediately} = \text{total alkalinity} \times \left[1 - \frac{\text{soil pH} - 1.5}{\text{plant pH} - 1.5} \right] \quad (6)$$

where a plant pH of 6.0 is assumed. This equation is based on Eq. (5) and assumes that following equilibration from a plant pH of 6.0 to the soil pH, part of the organic anions [(soil pH − 1.5)/(plant pH − 1.5)] remain intact and dissociated. These organic anions are then transferred to the labile and resistant soil fresh organic matter pools, where alkalinity is released upon further decomposition. Organic anions contained in feces are added to the resistant fresh organic matter pool as the feces degrade and enter the soil. Alkalinity associated with organic anion inputs of urine is released immediately and hence contributes, along with alkalinity released from plant residues, directly to the proton budget [Eq. (3)].

4.6 Cycles of Other Elements

A number of other nutrient cycles contribute to the proton budget, for example, redox reactions involving iron and manganese; weathering reactions involving Ca, Mg, K, P, and S; cation exchange; adsorption reactions; and formation of complexes with organic matter. The inorganic soil reactions in response to acid or alkali addition to the soil are not individually accounted for in the Helyar and Porter framework but are instead reflected in the pH buffer capacity used to convert the net proton production into a pH change. The only other cycle currently considered is the sulfur cycle in the GRAZPLAN soil acidity model. It optionally calculates the changes of the proton budget associated with sulfur oxidation/reduction using the same principles as outlined in Helyar and Porter [4]. The oxidation of 1 mole of elemental sulfur or organic sulfur to sulfate generates 2 moles of protons. The same amount of acidity is consumed when sulfate taken up by the plant is being reduced (see Sec. 4.3).

4.7 Lime Dissolution

Addition of lime is currently simulated only by APSIM-SoilpH. Lime dissolution is calculated from the size of the lime pool in a soil layer, the flow of water into the soil layer, and a function describing the solubility of lime as a function of soil pH. This function is a linear interpolation of dissolution data presented by Cregan et al. [66]. A lime dissolution submodel is also planned for the GRAZPLAN soil acidity model.

4.8 Net Mass Flow of Acidity

In both models, transport of acidity and alkalinity in the soil is calculated at each time step as the product of water flow and ion concentration. Ions involved are H^+, OH^-, HCO_3^-, CO_3^{2-}, and Al^{3+}. Activities of the first four ions are calculated using the constants of standard chemical equilibrium reactions [67]:

$$
\begin{aligned}
&H_2O \leftrightarrow H^+ + OH^- & &\log K = -14.00 \\
&CO_2(g) + H_2O \leftrightarrow H^+ + HCO_3^- & &\log K = -7.82 \\
&HCO_3^- \leftrightarrow H^+ + CO_3^{2-} & &\log K = -10.33
\end{aligned}
\tag{6a}
$$
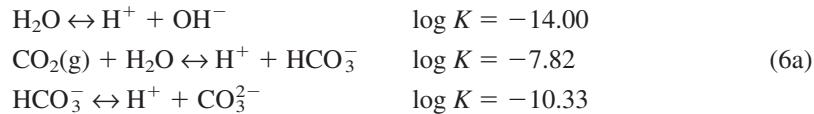
It is noted that at present the models do not simulate $CO_2(g)$ and, therefore, use a user-specified partial pressure of $CO_2(g)$ in the soil air. As the HCO_3^- and CO_3^{2-} concentrations are quite sensitive to the partial pressure of $CO_2(g)$ above pH 5.5, the input value for $CO_2(g)$ should take into account the expected level of biological activity in the soil in question.

Transport of aluminum is based on empirical equations. GRAZPLAN uses

$$
pAl_{tot} = 8.58 \times (pH - 2.84) / (pH - 1.35)
\tag{7}
$$

where pAl_{tot} is the negative $\log_{10}$ of the total activity of Al in the soil solution. This equation was fitted to data reported in Helyar et al. [68] and has, in a slightly different form, previously been used in the SPAM model [22,23]. APSIM-SoilpH uses a linear equation with parameters that are user defined and can be adjusted for soil type and difference between topsoil and subsoil

$$pAl = a \times pH + b \tag{8}$$

Depending on the experimental method used to determine a and b, pAl refers to the negative $\log_{10}$ of the activity of total Al or only Al^{3+}.

The preceding equations determine the activity of H^+, OH^-, HCO_3^-, CO_3^{2-}, and Al^{3+}. These are converted to concentrations using activity coefficients, which are calculated according to a simplification of the extended Debye–Hückel equation [69]:

$$\log \gamma_i = -AZ_i^2 \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.3\mu \right) \tag{9}$$

where γ_i is the activity coefficient of ion i, Z_i is its valency, A is a constant (0.509), and μ is the ionic strength of the soil solution. Currently the ionic strength is a constant, user-defined input. It is important that a value relevant to wet conditions is chosen, as this is when most transport occurs. The "net mass flow of acidity" term in Eq. (3) includes the HCO_{3ad} and HCO_{3ex} terms of Eq. (1). The HCO_{3ac} term of Eq. (1) is assumed negligible. Transport of CO_3^{2-} would be a minor component under most soil conditions but was added in APSIM-SoilpH to allow a future chemical description of lime dissolution. Future developments may also consider leaching of soluble organic molecules or organic matter movement between layers by soil fauna.

4.9 Choice of Method for Expressing pH

The definition of pH is the negative $\log_{10}$ of the activity of protons in solution. The pH of the soil solution is, however, not easy to determine experimentally. In practice most determinations of soil pH are therefore based on a soil extraction procedure. Several different ionic strengths and soil/extractant ratios have been used in the extraction procedures to minimize changes in the distribution of ions between the soil solution and the soil surfaces. The extract pH that best reflects solution pH and the relationships between different pH measurements are dependent on soil type [70–74].

The acidification models can, in principle, operate with pH determined by any method. However, there must be consistency between all parts of the model, including pH buffer capacity calculations. Thus, it is a user decision. In most cases this will be the pH in a 0.01 or 0.002 M $CaCl_2$ extract. Only when used in chemical equilibrium equations (e.g., for calculation of transport) should the pH really be that of the soil solution. For that purpose, either it needs to be assumed that ex-

tract pH approximates solution pH to an acceptable level or an equation that relates the two pH values needs to be used. As the latter equation would be soil type dependent, care needs to be taken that it forms a consistent set with the initial pH and pH buffer capacity values.

4.10 pH Buffering

The net acid addition [Eq. (3)] can be converted to a pH change using the pH buffer capacity of the soil [Eq. (2)]. The pH buffer capacity lumps together a number of proton-consuming processes such as cation exchange, mineral weathering, and formation of complexes with organic matter. The units of the pH buffer capacity are mol H^+ kg^{-1} (pH unit)$^{-1}$ and reflect the slope of a titration curve. As this slope is approximately constant between pH 4.5 and 6.0 [75], a single pH buffer capacity value is often used [4]. This single pH buffer capacity ignores the dissolution reactions of carbonate minerals and aluminum and iron hydrous oxides and hence should not be extrapolated to pH values above approximately 6.5 and below approximately 4.5. As can be expected given the nature of the buffering processes, the pH buffer capacity is soil specific and varies with factors such as cation exchange capacity, soil mineralogy, and clay and organic matter content. Several empirical regression equations have, therefore, been developed to predict the pH buffer capacity from more easily measured parameters, for example, organic matter and clay contents [76], organic carbon and clay contents [77–79], organic carbon, clay, and silt contents [13]. The effect of organic matter is particularly relevant, as organic matter contents can change quite dramatically over the longer time periods that are typically used in model simulations.

The structure of APSIM-SoilpH therefore allows regression equations to be built into the model. The parameters that are simulated by one of APSIM's modules (e.g., organic carbon content) can then change the pH buffer capacity dynamically as part of the simulation. The rapid increase in buffering at low pH (< 4.0) due to aluminum dissolution is described as a function of exchangeable aluminum. User input of pH buffer capacity is also possible.

In the GRAZPLAN soil acidity model, the soil pH buffer capacity is computed as the sum of three terms. The first term represents the buffering capacity of the soil mineral phase, which remains constant during the simulation. The second term represents the buffering capacity of the soil organic carbon and shifts in response to changes in the organic carbon content of the soil. The third term varies with the concentration of Al^{3+} in the soil and takes account of the buffering processes due to enhanced dissolution of soil minerals at low pH values. In order to parameterize a simulation, the user needs to specify the initial soil pH buffer capacity and the pH buffer capacity of the organic matter. If there are no measured values available, the software offers the option of estimating values based on empirical equations. The initial soil pH buffer capacity, the initial carbon content, and

the initial pH are then used to estimate the constant pH buffer capacity term at the start of the simulation.

Time is an important factor in pH buffering processes. For the same total acid production, a high acid production rate will cause a larger pH drop than a slow acid production rate [80]. Although the pH buffer capacity is defined as "the measure of the rate of acid or alkali addition per unit change in soil pH" [4], the word "rate" in this definition does not have a time aspect. Time is a factor only in the experimental determination: the time of equilibration, which may affect the experimental results. Although it has been acknowledged that this is a factor of uncertainty in the application of the Helyar and Porter framework [12–15], little attention has been given to the fact that the pH buffer capacity that is used must be appropriate for the time scale of the period over which the net acid production was determined. For models, such as APSIM-SoilpH and the GRAZPLAN soil acidity model, that generally operate on a daily time step, this issue may be more critical than for the longer term experimental applications of the Helyar and Porter framework. Currently, the models use a daily time step for the calculation of the net acid production and pH change, which is shorter than that of most experimental methods used to determine the pH buffer capacity. The implications that this may have will need to be studied further. It may be necessary to increase the calculation time step, or it may prove more appropriate to distinguish buffer rate and buffer capacity, concepts introduced by Kauppi et al. [81] (RAINS model). They defined the buffer rate as "the maximum potential rate of the reaction between buffering compounds and the hydrogen ions" and the buffer capacity as "the gross potential, the total reservoir of the buffering compounds." The distinction between the two terms allowed them to capture situations where buffer capacity was high but the buffer rate limited proton consumption.

This discussion highlights the (current) uncertainty in the choice of an appropriate buffer capacity for use in simulations. As pointed out by Ridley et al. [14] and Porter et al. [15], uncertainty in pH buffer capacity may be a reason for the wide variability in acidification rates reported in the literature. The advantage of the models is that the effects of uncertainty in model input can be easily assessed via a sensitivity analysis. Uncertainty bounds can then be specified for model outputs. It is important to remember that there will not necessarily be a linear relationship between uncertainty in the pH buffer capacity and uncertainty in predicted pH change. The model includes various feedbacks (see next section), which will make this a nonlinear function. Uncertainty bounds will strongly depend on the scenario of the simulation (weather, soil type, management).

4.11 Feedbacks in the Models

Soil pH affects several processes that are represented in the APSIM and GRAZ-PLAN models. These include processes described in the acidity models (dynam-

ics involving organic anions, lime dissolution, transport of acidity) but also processes in the soil nitrogen models. For example, urea hydrolysis is influenced by pH, as is nitrification. In the latter case, the pH feedback provides a natural limitation of acidification due to the nitrogen cycle. Nitrification will progressively slow down when the pH drops below pH 6 and is assumed to cease completely at about pH 4.5 (user input in APSIM). Acid production by this key process of the nitrogen cycle will, therefore, stop as well. The rising ammonium concentration may lead to increased ammonium uptake with a corresponding increase in excretion of protons. Compared with the situation of nitrification and nitrate uptake in the same layer, this does not have an effect on the proton budget, but when contrasted with the situation of nitrate leaching out of the layer, there is still a reduction in acid production.

Crop feedback is not yet included in the models, and in instances where "tolerant" plants are being simulated, feedbacks may have little relevance. It is likely to be critical for long-term runs where the soil acidifies strongly or where "sensitive" species are being simulated. It is, however, not a straightforward matter, as there are many ways in which acidification can negatively affect crop growth (H, Al, Mn toxicity; inhibition of Mg, Ca, and K uptake; decrease in P and Mo solubility; inhibition of root growth [82]). The most influential factors are likely to vary from crop to crop, but aluminum toxicity will often be one of them. It appears that aluminum toxicity does most of its damage by impairing root growth and function in a small zone just behind growing root tips. Presumably, there is no simple function that predicts aluminum damage to roots or the influence of tolerance mechanisms.

5 CASE STUDY 1—ACIDIFICATION UNDER WHEAT: SIMULATIONS WITH APSIM-SOILPH

To illustrate the use of APSIM-SoilpH, we present simulations of the wheat experiment reported in Poss et al. [17] and compare model outputs with their assessment of acidification in this system. As the experiment covered only one cropping season, we use the model to extrapolate in time in order to determine how representative the 1993 year was. The model is also used to study the pH profile development over a 12-year period and to determine the effects of fertilizer management.

5.1 Experiment Reported by Poss et al. (1993)

The experiment was conducted at Charles Sturt University (CSU) near Wagga Wagga, New South Wales, Australia. The field was sown to wheat (*Triticum aestivum* L. cv. Janz) in 1993. Details of the experiment are given by Poss et al. [17], Dunin et al. [83], and Smith et al. [84,85]. Briefly, wheat was sown on June 6,

1993 in two adjacent 5-ha areas identified as the fertilized and unfertilized treatments. Both received diammonium phosphate (DAP, 17 kg N ha^{-1}, 25 kg P ha^{-1}) drilled with the seed at sowing, but only the fertilized treatment received a top dressing of 140 kg N ha^{-1} as urea on August 6, 1993. The crop was harvested on December 9, 1993. Prior to sowing, the surface residue of the previous wheat crop was burned (March 31, 1993), the ashes and unburned straw being incorporated (April 15, 1993). Weeds were most likely present during the fallow, but no details on date of appearance or cover were available.

The soil was a red kandosol [86] (previously known as a red earth). Its texture changes from sandy clay loam in the surface (0 to 15 cm) to medium clay in the subsoil. The B horizon has limited structure and a low permeability. The soil is common in the Wagga Wagga district [87]. Soil water and mineral nitrogen contents were measured at regular intervals, as well as crop growth and nitrogen uptake. Both the fertilized and unfertilized treatments contained a weighing lysimeter and were instrumented with ceramic suction cups [88] and time domain reflectometry (TDR). Net mineralization rates of the topsoil (0 to 10 cm) were determined by in situ incubations [85]. Cumulative water flux and nitrate leaching at 25 and 90 cm were calculated from lysimeter and TDR results combined with solution nitrogen contents [17,83,84,88]. To calculate the various proton budget terms [Eq. (1)], measurements were also made of the amount and ash alkalinity of surface residue, crop nutrient concentrations, pH and nitrate concentration of rain, and soil aluminum and manganese concentrations. In addition, the pH buffer capacity was determined [17].

5.2   Parameterization of the Model

For the simulations presented here we used APSIMv1.6 configured with the SoilpH module, the Soilwat2 water balance module, the Nwheat crop module, the SoilN2 soil nitrogen module, and the Residue2 surface residue module. The Manager and Operations modules were used to simulate soil and crop management.

The simulations started on December 15, 1992 after the harvest of the previous wheat crop. Locally measured daily rainfall was available from June 1993. Data from the nearby NSW Agricultural Research station were used prior to that date. Maximum and minimum temperature and radiation data were from the Wagga Wagga Meteorological Office at Forest Hill (located approximately 25 km from the experimental site).

The soil profile (0 to 2 m) was divided into 10 layers, the first of which was 0 to 10 cm. Profiles of the lower limit and drained upper limit for the water balance calculations of the SoilWat2 module were obtained from the driest and wettest profiles observed during the 1993 fallow and cropping season. This resulted in 30.5 mm total plant-available water in the topsoil (0 to 25 cm) and 65.5 mm in the subsoil (25 to 90 cm). Saturation values were obtained from in situ mea-

surements following ponding. The initial water content profile was based on measurements made on March 3, 1993. This assumes no increase in soil water storage from December 15 until March 3. The simulation confirmed that indeed all rainfall during this period was lost through evaporation. A runoff curve number of 75 was chosen on the basis of the sandy clay loam texture of the topsoil. Diffusivity constants (44 and 16) were those appropriate for the clay subsoil. To obtain close agreement with the evaporation data obtained from the lysimeters, it was necessary to use different evaporation parameters (U and cona) for winter (2 and 2) and summer (6 and 3.5) conditions. Others have made similar observations (N.I. Huth and S. Asseng, personal communication, 2000), notably that the rate of second-stage evaporation is not independent of evaporative demand.

Profiles of bulk density, initial organic carbon, and pH were as measured at the site in 1993. Low initial mineral nitrogen content was assumed, on the basis that most nitrogen would have been taken up by the 1992 crop. The CO_2 partial pressure in the soil was assumed to be 0.3 kPa [67]. Parameters of the pAl-pH relationship [Eq. (8)] were based on data from a field experiment near Wagga Wagga (K. R. Helyar et al., unpublished). The initial weight of surface residues (11 t ha^{-1}) was an estimate based on the size of the previous crop. It was slightly higher than the 9.7 t ha^{-1} reported by Poss et al. [17] as this measurement was made in March, 3 months into the fallow. Ash alkalinity of surface residues, pH buffer capacity, and pH of rainfall were taken from Poss et al. [17]. Nutrient concentrations in the crop were those measured at harvest. The initial root residues and their C/N ratio were estimated on the basis of the size of the crop in 1992 and typical values obtained in a 12-year continuous wheat simulation (see later). The last two parameter values are a source of uncertainty in this simulation. The urea application in the fertilized treatment was reduced to 120 kg N ha^{-1} to allow for volatilization losses that were not accounted for by the model (estimated to be 10 to 25 kg N ha^{-1} [85]).

Standard values were chosen for the model constants in Soilwat2, SoilN2, and Residue2 [26], with the following exceptions. Like Asseng et al. [43] and Snow et al. [89], we found it necessary to increase the magnitude of parameters controlling potential mineralization. We chose to use the value of 0.00025 day^{-1} of Snow et al. [89] for the potential decomposition rate for the humus pool (*rdhum*) and increase the daily potential decomposition rate for the soil biomass pool (*rdbiom*) in proportion to 0.0135 day^{-1}. The potential decomposition rate of residue was lowered to 0.02 day^{-1}, down from the 0.1 day^{-1} proposed by Probert et al. [26] based on a study at Warra, Queensland. The higher value required in Queensland seems to be associated with the relatively few days that are predicted to have adequate moisture for decomposition to proceed. In addition, the efficiency of carbon retention upon decomposition of organic matter or residues was reduced from 40 to 30%, which effectively reduces the immobilization demand when cereal residues decompose. This was based on experiences at other locations

(M. E. Probert et al., unpublished) where a tendency has been found for the model to underpredict mineralization and crop uptake of nitrogen if large amounts of cereal residues are present.

APSIMv1.6 does not have a standard module for weeds. We, therefore, reconfigured the Nwheat module to represent a grassy weed species. This was achieved by eliminating carbon allocation to grain, selecting an extended time to flowering, and limiting rooting depth to 50 cm. A similar approach to simulating the effects of weed competition in a maize rotation has been reported by Keating et al. [90]. Fischer et al. [91] also used a modified wheat model (WEEDGRO) to simulate weed growth during fallow periods in wheat systems in southern New South Wales. The weed germination scheme was adopted from Fischer et al. [91], with weeds germinating on the first rain event after December 1 that exceeded 25 mm (December to February) or 20 mm (March to April 10) over two consecutive days. Weeds were killed and incorporated at the tillage event on April 15. Fischer et al. [91] allowed weed growth in May as well. They found that their scheme correctly predicted 14 out of 18 experimentally observed waves of weed emergence.

As no experimental details on weed growth were available and parameterization of the model was not fully independent of the data used to evaluate the performance of the model, the simulations are not a validation of the model. The simulations are, however, still suitable for testing confidence in the model's description of water and nitrogen cycling due to the extensive and detailed nature of the experimental data set, which includes information on distributions of water and nitrogen in the soil profile as well as fluxes such as evapotranspiration, nitrate leaching, mineralization, and uptake of nitrogen. Thus, there are adequate data to ascertain that the model is simulating the important processes involved in the dynamics of soil water and nitrogen with an acceptable degree of accuracy.

5.3 Simulation of Experimental Data and Comparison with Observations

The simulation results for the unfertilized and fertilized treatments were compared with the measured profiles of water content and mineral nitrogen during 1993. Changes in water and nitrogen contents and the movement of nitrate within the profile were simulated satisfactorily (data not shown). Agreement with measured evapotranspiration was also reasonably good, except for a small underprediction at the end of the season in the unfertilized treatment. Patterns of cumulative water flux and nitrate leaching, therefore, compared well with the data presented by Poss et al. [17] and Smith et al. [84] (Fig. 6).

The effect of weeds during the preseason fallow in 1993 was small. The largest effect was on nitrate leaching past 25 cm, which was predicted to accumulate to 40 kg N ha^{-1} in the absence of weeds, still within the maximum observed range (not shown). The weeds germinated on December 27, 1992, emerged 4 days
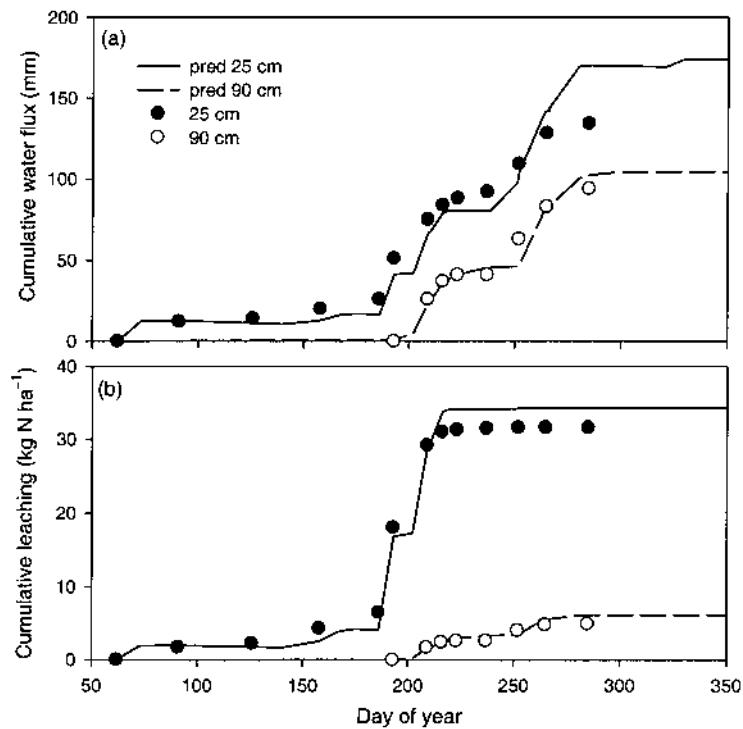
FIGURE 6 Comparison of values based on observed data (symbols) and model predictions (lines): (a) cumulative water flux at 25 and 90 cm depth (unfertilized treatment) and (b) cumulative nitrate leaching at 25 and 90 cm depth (unfertilized treatment). Observed data points from Poss et al. [17] and Smith et al. [84].

later, and reached a maximum leaf area index (LAI) of 0.037 and a maximum aboveground biomass of 230 kg ha^{-1}.

The patterns of crop growth [85] were simulated satisfactorily. Predicted dry matter biomass (8.6 t ha^{-1}) and grain yield (3.3 t ha^{-1}) of the unfertilized treatment were slightly below the measured values (10.9±1.7 and 3.8±0.7 t ha^{-1}, respectively; mean ± SD). The values of the fertilized treatment (biomass of 17.4 t ha^{-1} and grain yield of 6.2 t ha^{-1}) compared well with those measured (16.1±1.0 and 6.8±0.9 t ha^{-1}, respectively). Nitrogen uptake by aboveground biomass was comparable in the unfertilized treatment (70 predicted vs. 72±18 kg N ha^{-1} measured) and slightly high in the fertilized treatment (176 vs. 165±16 kg N ha^{-1}). Total mineralization for the fallow and cropping season was 150 kg N

ha^{-1}. Mineralization during the cropping season was predicted to be 52 kg N ha^{-1} in the surface 10 cm.

The proton budget predicted by the model highlights the different rates of acidification of the topsoil and subsoil (Table 2). In both the fertilized and unfertilized treatments, the topsoil (0 to 25 cm) acidifies and the subsoil undergoes a net alkalinization. The nitrogen cycle is the main cause of acidification in the topsoil.

Net proton excretion by roots is important as well, largely due to the prediction of significant uptake of ammonium. Poss et al. [17] estimated a much smaller contribution of ammonium uptake, which was limited to the subsoil (Table 2). Experimental data on the form of nitrogen uptake were not available. The Nwheat module uses an uptake routine similar to that of CERES-Wheat [92], in which soil supply of nitrate and ammonium is a function of their concentrations in the soil. With most mineralization occurring in the topsoil, this is where the model predicts most ammonium uptake. However, because the source of the nitrogen was largely organic nitrogen and urea (reference forms in the Helyar and Porter framework, Fig. 2), the form in which nitrogen is taken up has no effect on the proton balance when uptake occurs in the same layer as nitrification. It affects only the relative magnitudes of the nitrogen cycle and root excretion terms. In the case of the fertilized treatment, a dry spell shortly after the urea application and rapid uptake by the crop minimized nitrate leaching, so that the effect on the proton balance would be minor.

Total nitrogen uptake was higher than presented in the proton budget of Poss et al. [17] (Table 2) because they considered only uptake by aboveground biomass, whereas the model predictions included nitrogen uptake by roots. This also accounts for the enhanced alkalinization of the subsoil. The main source of alkalinity in the topsoil is returned residues. The model predicts a small role for the depletion of organic anions. This may be explained by the fact that the proton budget presented here included the return of root residues, which limited the decline in soil carbon.

Similar to the findings of Poss et al. [17], the contribution of mass flow was small. This term would, however, become more important if the topsoil acidified further. Despite small differences in the proton budget terms, in general the simulations are consistent with the assessment of Poss et al. [17] that whereas overall profile acidification was small, acidification occurred in the topsoil.

5.4   How Representative was 1993?

Detailed experiments such as the one presented by Poss et al. [17] can be carried out for only a limited period and hence will sample only a small fraction of the weather patterns. To check how representative the experimental year 1993 was, we ran a long-term simulation scenario based on historical weather data (SILO

TABLE 2 Proton Budget (kmol H$^+$ ha^{-1}) Predicted for the Period December 15, 1992 to December 15, 1993

Budget term	APSIM-SoilpH simulation				Poss et al. [17] analysis: selected terms			
	Unfertilized		Fertilized		Unfertilized		Fertilized	
	0 to 25 cm	25 to 90 cm	0 to 25 cm	25 to 90 cm	0 to 25 cm	25 to 90 cm	0 to 25 cm	25 to 90 cm
Nitrogen cycle effects	4.8	0.9	4.7	0.8	6.0	0.2	13.8	0.1
Root excretion	0.1	−2.9	1.4	−2.6	−1.7	−0.4	−6.6	−0.4
NO$_3^-$ uptake	−3.8	−3.3	−7.4	−3.5	−3.0	−1.6	−10.7	−1.6
NH$_4^+$ uptake	2.6	0.0	6.3	0.0	0.0	0.5	0.0	0.5
Cation excess	1.2	0.4	2.5	0.9	1.3	0.7	4.1	0.7
Returned organic anions	−2.7	0.0	−2.7	0.0	−1.8	0.0	−1.8	0.0
Depletion of organic anions	−0.7	−0.1	−0.4	−0.1	−1.6[a]	−1.1[a]	−1.6[a]	−1.1[a]
Net mass flow of acidity	0.0	0.1	0.0	0.1	0.2	0.3	0.2	0.3
Total	1.5	−2.0	3.0	−1.8	1.1[a]	−1.0[a]	3.9[a]	−1.1[a]

[a] Values for depletion of organic anions and for Total of Poss et al. analysis are based on a 2% per year mineralization rate of organic matter, as the experimental rate of mineralization (3.5% per year) was probably an overestimate [17,85].

Patched Point Dataset*) from the Meteorological Office at Forest Hill close to the experimental site. The simulation consisted of repeating the preceding scenario of a wheat crop following a summer fallow each year from 1958 to 1997. In the simulations, wheat was sown within a window from May 1 until June 15. The conditions for sowing included 30 mm rain in the last 10 days, less than 1 mm rain the previous day, no rain on the day, and soil water in the 10- to 15-cm layer exceeding 50% of plant-available soil water storage. If no sowing opportunity arose before June 15, the crop was sown "dry" on that day. Fertilizer management reflected the 1993 experiment with 17 kg N ha^{-1} ammonium applied at sowing as DAP and 120 kg N ha^{-1} as urea 62 days later (fertilized scenario only). The crop was harvested 12 days after maturity (as in the 1993 experiment), after which crop residues were left on the surface. These were 95% burned on March 31 and the remainder incorporated on April 15. Weeds were allowed to germinate following the scheme of Fischer et al. [91] (see earlier). Soil and crop parameterizations were identical to those of the 1993 simulations. Soil water, soil nitrogen, surface residue, and soil pH parameters were reset after every harvest to the conditions that existed after the harvest in 1992 so as to focus on the effects of weather patterns during the fallow and crop on proton-producing and proton-consuming processes without the confounding effects of carryovers from the previous season.

Rainfall in 1993 at the experimental site was significantly lower than that at Forest Hill, which is approximately 25 km away (592 mm vs. 733 mm). As shown in Table 3, the higher rainfall particularly affected the cumulative water flux and nitrate leaching below the root zone ($\geq$ 70% increase). Nitrate leaching at 25 cm was affected less. Acidification of the topsoil was, therefore, only slightly higher ($\leq$ 20% increase).

The year 1993 was a very wet year within the 1958 to 1997 rainfall record of Forest Hill. Annual rainfall exceeded the 85th percentile, and monthly rainfall during July (130 mm), September (121 mm), and November (97 mm) exceeded the 90th percentiles for these months. Cumulative water flux at both 25 and 90 cm was, therefore, above average (both 76th percentile). Despite the relatively dry weather in August (27 mm, 17th percentile) and the rapid nitrogen uptake by the crop following the urea application, the amount of nitrate that leached past 25 cm still ranked at the 79th percentile (Fig. 7). Timing of fertilizer application in relation to crop nitrogen demand is, however, a critical factor in determining nitrate leaching. The large amount of nitrate leached in 1976 illustrates this. Rainfall during 1976 was below average, with very little rain from March until August (66

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* SILO is a meteorological information service for rural industries (www.bom.gov.au/silo/). As part of this service, the Patched Point Dataset was developed by the Queensland Department of Natural Resources. It combines original Bureau of Meteorology measurements for a particular station with interpolated data to provide a continuous meteorological data set. For more information, see http://www.dnr.qld.gov.au/silo/

TABLE 3 Selected Model Outputs for the Period December 15, 1992 to December 15, 1993 Using Two Different Rainfall Records (Distance Approximately 25 km)

	Local rainfall		Forest Hill Met station	
Model output	Unfertilized	Fertilized	Unfertilized	Fertilized
Rain (mm)	592	592	733	733
Evaporation (mm)	309	278	331	297
Transpiration (mm)	158	279	144	301
Cumulative water flux at 25 cm (mm)	174	151	274	228
Cumulative water flux at 90 cm (mm)	104	63	178	138
Nitrate leaching at 25 cm (kg N ha^{-1})	34	36	40	45
Nitrate leaching at 90 cm (kg N ha^{-1})	6	4	12	11
Net acidification in the 0 to 25 cm layer (kmol H$^+$ ha^{-1})	1.5	3.0	1.7	3.6
Net acidification in the 25 to 90 cm layer (kmol H$^+$ ha^{-1})	−2.0	−1.8	−1.9	−1.9
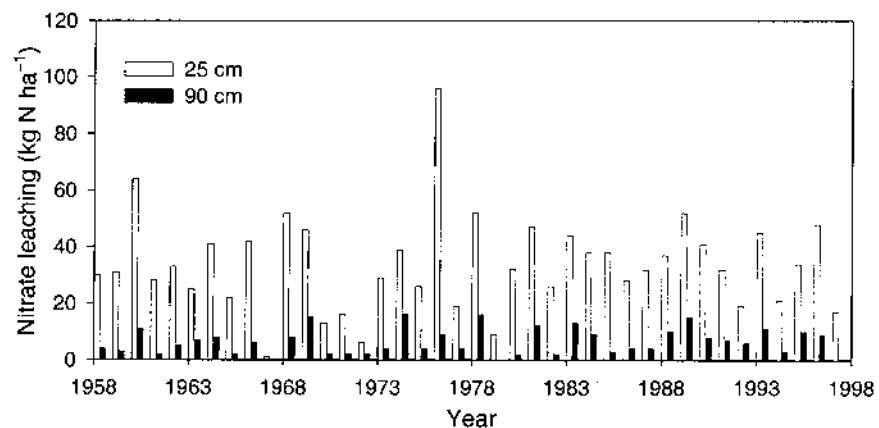
FIGURE 7 Variation in simulated annual nitrate leaching at 25 and 90 cm for the fertilized scenario based on the Forest Hill meteorological record. Note that every year conditions were reset to those measured after the 1992 crop.

mm). In the simulation scenario this led to late sowing and poor crop establishment. Because urea application was fixed at 62 days after sowing, this occurred not long before the above-average September rainfall and led to significant leaching from the topsoil.

In the fertilized treatment, acidification of the topsoil is highly correlated with nitrate leaching past 25 cm (0.86 correlation coefficient), causing the acidification rate of the topsoil in 1993 to be above the average, although not as high as in, for example, 1976, despite the much higher rainfall. Compared with the average rates of 1.0 kmol H^+ ha^{-1} $year^{-1}$ for the unfertilized scenario and 2.5 kmol H^+ ha^{-1} $year^{-1}$ for the fertilized scenario, acidification in the 0 to 25-cm layer in 1993 was ranked at the 79th and 84th percentiles.

The ranking of 1993 is sensitive to the assumptions made about weed growth in the simulations. When weed-free fallows were assumed (data not shown), the simulations ranked the year 1993 at the 66th and 71th percentiles for topsoil acidification in the unfertilized and fertilized treatments, respectively. The presence of weeds during the fallow keeps the soil drier and hence influences acidification through reduced drainage and nitrate leaching at the break of season. It may also affect preseason mineralization. As the period January to April was relatively dry in 1993, growth of weeds was predicted to be limited (maximum LAI of 0.053 and aboveground biomass of 314 kg ha^{-1}), compared with the long-term average and maximum values for LAI (0.21 and 0.81) and aboveground biomass (587 and 2619 kg ha^{-1}). A greater impact of weeds is expected in years with relatively wet fallow periods, so that topsoil acidification in these years is reduced most.

Although the weed growth simulations have been only indirectly tested against evapotranspiration data of the Poss et al. 1993 experiment [17], we nevertheless expect that the simulated level of weed activity is not unrepresentative for cereal systems with similar fallow management. In reality, weed growth, of course, remains highly site specific due to its dependence on fallow management. The preceding analysis should therefore be viewed in the specific context of the chosen scenario. In addition to the uncertainty introduced by weeds, carryover effects, which were excluded from these simulations, may affect carbon and nitrogen dynamics and hence soil acidification.

5.5 Topsoil pH Decline and pH Profile Development under Continuous Wheat

The net proton production or consumption in each layer (kmol H^+ ha^{-1} $year^{-1}$) is converted by the model into a pH change using the pH buffer capacity [Eq. (2)]. Continuous simulation scenarios (without resetting) were, therefore, carried out to study the pH profile development under wheat. These scenarios mimicked the conditions of the Poss et al. experiment [17], with an unfertilized (only DAP at sowing, 17 kg N ha^{-1}) and a fertilized treatment (DAP, 17 kg N ha^{-1}, and top

dressing of urea). A third scenario was included in which no fertilizer was added (N0 treatment).

The pH profile measured in 1993 [17] followed 9 years of cropping and one liming event (1991). It had an acid layer between 10 and 15 cm with a pH ($CaCl_2$) of 4.5. The pH values of topsoil (0 to 5 cm) and subsoil (70 to 90 cm) were both 5.8. To study how such a pH profile might develop, the initial pH profile for the continuous run was modified to start at 4.9 in topsoil (0 to 10 cm), gradually increasing to 5.1 at 15 to 25 cm and to 5.8 at 50 cm and below. The topsoil pH values match those reported by Heenan and Taylor [93] and Conyers et al. [94] for the start of a cropping rotation trial. Model initialization, crop, soil, and fallow management were otherwise the same as for the scenarios already discussed. To allow the pH buffer capacity to change over time, the model calculated the pH buffer capacity as a function of pH, exchangeable aluminum, effective cation exchange capacity, and the organic carbon fraction [95–97].

The period 1979 until 1991 was chosen to allow a qualitative comparison with data from a 12-year field trial of the effect of management practices on soil pH decline carried out on a similar soil near Wagga Wagga [93,94]. Two of their treatments were continuous wheat with (WW+N) or without (WW−N) fertilizer (100 kg N ha^{-1} year^{-1}).

In both the unfertilized (DAP) and fertilized (DAP+urea) scenarios, the pH of the topsoil (0 to 10 cm) was predicted to decline steadily (Fig. 8). In the unfertilized treatment, the rate of decline was smaller than in the fertilized treatment. The pH decline of the fertilized scenario compared well with the data presented by Heenan and Taylor [93] for their fertilized treatment (WW+N). Without any fertilizer (N0), the pH of the topsoil did not decline in the simulations. This behavior differed from that of the unfertilized treatment (WW−N) of Heenan and Taylor [93], which was more similar to the DAP treatment, especially in the first 6 years. This is most likely due to differences in initial soil fertility. The experiment of Heenan and Taylor [93] was preceded by 19 years of mostly subterranean clover–based pasture, which would have increased the more labile components of organic matter significantly. Indeed, parallel measurements of soil organic carbon and nitrogen in the unfertilized (WW−N) treatment showed a marked decline in both carbon (6 t ha^{-1} over 14 years) and nitrogen (0.7 t ha^{-1} over first 12 years) [98]. These levels of mineralization could not be simulated by the model, which was initialized based on conditions that existed after the harvest in 1992. Reparameterization of the model was considered beyond the scope of this case study. It is interesting to note, however, that the leveling out of pH decline in the later years of the experimental WW−N treatment, when fertility had run down, was similar to the simulated N0 treatment.

Simulation of pH profiles requires specification of very thin layers near the surface due to the rapid changes in pH over the first 15 to 20 cm (e.g., see data from Conyers et al. [94] in Fig. 9). This presented a slight problem for the APSIM con-
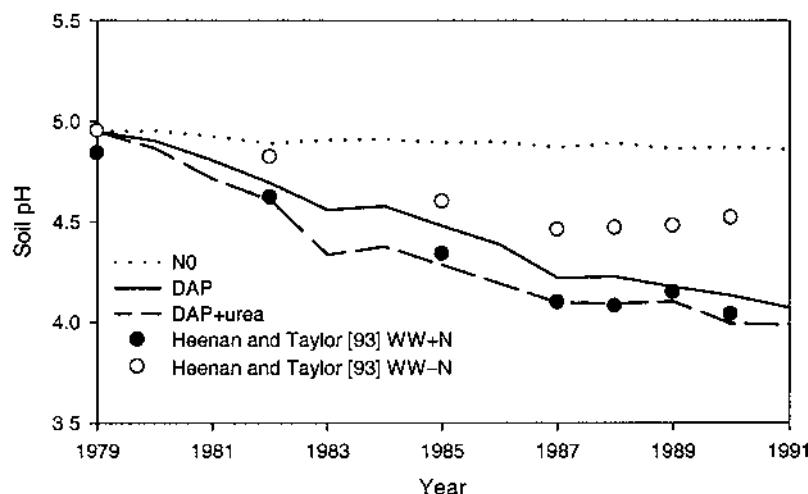
FIGURE 8 The effect of fertilizer application on the predicted decline in topsoil (0 to 10 cm) pH (lines) and a qualitative comparison with data from similar treatments presented by Heenan and Taylor [93] (symbols). Treatments: N0 = continuous wheat with no fertilizer application, DAP = continuous wheat with 17 kg N ha^{-1} at sowing as DAP, DAP+urea = continuous wheat with 17 kg N ha^{-1} at sowing as DAP and 120 kg N ha^{-1} topdressing as urea, WW+N = continuous wheat with 100 kg N ha^{-1} as urea (three-way split at sowing, midtillering, and flowering), and WW−N = unfertilized continuous wheat.

figuration used here. In the Soilwat2 water balance module, evaporation currently occurs only out of the first layer. Although the drying front can extend beyond this depth due to upward water flow, in some soils this can present problems when layers as thin as 5 cm are chosen. This proved to be the case for the soil from the experiment considered here with its texture contrast between topsoil and subsoil. During the simulation of the summer fallows, the drying front did not extend deep enough, keeping in particular the second and third layers too wet. As a consequence, the mineralization in these layers was predicted to occur earlier than happened in reality, leading to overpredictions of nitrate leaching past 25 cm. The predicted pH profiles presented in Fig. 9 were, nevertheless, obtained using thin 5-cm topsoil layers (0 to 5, 5 to 10, 10 to 15). Due to the overprediction of nitrate leaching, the pH drop in the surface layers is slightly overpredicted, but otherwise the results are consistent with the experimental data presented by Conyers et al. [94].

The problem with thin surface layers may not manifest itself with all soils. Asseng et al. [43] have presented successful simulations of nitrate leaching in a deep sand using the same 5-cm surface layers. The problem could be overcome by

configuring APSIM with the SWIM water balance module, which is based on a numerical solution that would actually improve with thinner layers [27].

5.6 Further Comments

Poss et al. [17] suggested that wheat cropping may have contributed little to the observed acidification in the Wagga Wagga region and instead implicated the ley phase in combination with fallow breaks. They arrived at this conclusion by generalizing their findings for 1993, when they observed limited nitrate leaching below the root zone and little overall acidification of the profile despite high rainfall and high drainage. However, whereas the acidification under cropping may be small on a whole profile basis, the proton budget (Table 2) and the data of Heenan et al. [93,94] (Figs. 8 and 9) show that in the zone that matters for crop establishment and early growth (surface 0 to 25 cm) acidification can be significant, especially under fertilized conditions.

The simulations describe the pH profile development under wheat reasonably well, despite the fact that they have not been parameterized specifically for the Heenan et al. cropping trial [93,94]. Although preliminary, the results show that, following additional testing, the model could be a useful tool to explore the
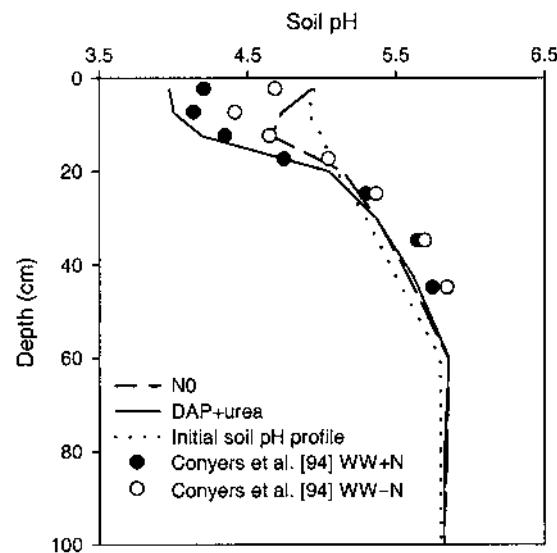
FIGURE 9 The effect of fertilizer application on the predicted pH profiles after 12 years of continuous wheat (lines) and a qualitative comparison with data from similar treatments presented by Conyers et al. [94] (symbols). Treatments as in Fig. 8.

relative contributions to soil acidification of crop and ley phases and the importance of any carryover effects. Testing should focus on the current uncertainties in model parameterization and on the transition from ley to cropping phase. It should consider processes in the subsoil, as the ley phase could be important for deeper acidification, as shown in the next case study (Sec. 6). Such analyses of crop and ley phases would be particularly relevant given the push in recent years to introduce lucerne in cropping rotations to reduce deep drainage. It is important that this introduction is accompanied by management practices that will minimize the effects on soil acidification. Simulation modeling may assist in exploring management options and designing a sustainable rotation.

6 CASE STUDY 2—ACIDIFICATION UNDER PASTURE: SIMULATIONS WITH THE GRAZPLAN SOIL ACIDITY MODEL

This study illustrates the application of the GRAZPLAN soil acidity model to data from the landmark research of Bromfield et al. [21] on soil acidification under subterranean clover–based pastures in the catchment of the Pejar dam, near Crookwell, New South Wales, Australia. They reported that substantial acidification had occurred in a number of soils under long-established pastures. The extent of the decline in soil pH was associated with the length of time since the pastures were established; the largest decline was seen in yellow podzolic soils derived from granite. The case study also demonstrates that the GRAZPLAN soil acidity model can be applied to understanding the relative importance of the processes contributing to soil acidification. It illustrates some of the issues yet to be resolved in modeling these processes and indicates where further research is required.

6.1 Data Inputs for the Simulation

Bromfield et al. [21] measured soil pH in 1980 in pastures established between 26 and 55 years previously and compared the values with those for sites under unimproved native vegetation. When estimating the changes in soil properties with time under pasture, they assumed that the values at the unimproved sites represented the situation 55 years previously. The same assumption was made in the simulation study. Simulations of pasture production on the yellow duplex soil derived from granite, described by Bromfield et al. [21], were made for the period from 1925 to 1980 to mimic the development of soil pH profiles beneath 55-year-old subterranean clover pastures. A wool-growing enterprise was assumed, stocked continuously at nine Merino wethers per hectare with a 20% replacement policy. A minimal feed supplementation policy was selected with wheat fed to the sheep if their condition score fell below 1.0. The pastures in the study area would have comprised mainly annual grasses and subterranean clover, and this was the species composi-

tion assumed in the simulation with the parameter set for the clover cultivar Mt. Barker used. The assumed rate of superphosphate application was 125 kg ha^{-1} year^{-1} (9% P content). This was calculated from the rate of increase of total phosphorus in the soil [99] and assuming that 50% of applied phosphorus remained unused in the soil profile. The weather file used to run the simulation was based on Bureau of Meteorology data for Crookwell and nearby localities. For the period from 1957 to 1980 weather data were constructed using the Queensland Department of Natural Resources Data Drill* facility. For the period prior to 1957, radiation and temperature data were generated using Richardson's [100] generator.

Soil horizon depths, pH buffer capacity, and clay contents were those for soil profile "H" described by Bromfield et al. [21]. The A horizon boundary was set at 40-cm depth on the basis of the change in the clay content. Hydraulic properties were not recorded in the original study and were assumed to be similar to properties measured for a granite-derived, yellow podzolic soil at the Ginninderra Experiment Station, near Hall, Australian Capital Territory, Australia. Phosphorus sorption characteristics of this topsoil were also used in the simulation. Soil bulk densities used in the simulation were the same as in Helyar and Porter [4]. Soil organic carbon, nitrogen, and phosphorus contents were estimated using the equations relating time under pasture to soil nitrogen and phosphorus contents from a study on a similar soil nearby at Binda, New South Wales, Australia [99]. The C/N ratio of soil organic matter was assumed to be 10:1. The initial values for soil pH buffer capacity were deduced using the initial calculated carbon values and a soil organic carbon buffer capacity of 1.44 mol H$^+$ kg^{-1} C.

The pH and pH buffer capacity (pHBC) values for soil profile H reported by Bromfield et al. [21] were measured in 1:5 soil/water suspensions. These were converted to pH(CaCl$_2$) and pHBC(CaCl$_2$) values because the calculations in the GRAZPLAN soil acidity model are based on values measured in 0.01 M CaCl$_2$. This was based on equations shown in Bromfield et al. [21].

6.2 Production Summary

Average pasture production was predicted to be 7.2 t DM ha^{-1} year^{-1} (range 2.4 to 19 t ha^{-1} year^{-1}). Owing to the effect of phosphorus fertilizer inputs, productivity trended upward from 4.8 to 10 t ha^{-1} year^{-1} over the 55 years of the simulation. The average species composition was 36% clover and 64% annual grasses. The average wool clip was 42.1 kg greasy ha^{-1} year^{-1} and average net export of sheep live weight was 65.7 kg ha^{-1} year^{-1}. These are considered to be reasonable figures for production in that district.

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* The SILO Data Drill was developed by the Queensland Department of Natural Resources and provides interpolated data for any location in Australia. For more information, see http://www.dnr. qld.gov.au/silo/

6.3 Accumulation of Carbon and Nutrients

Figure 10 shows simulated and measured values of the total nitrogen, organic phosphorus, and total phosphorus content of the soil. The simulated rates of increase in the three nutrient pools were in reasonable agreement with the changes reported by Williams [99].

The slower increase in total nitrogen simulated in the first 25 years and the accelerated increase thereafter were associated with lower and higher pasture yields in these periods, respectively. The higher yields in later years were due to several factors, including improved availability of phosphate as a result of regular fertilizer inputs, increases in soil nitrogen input from the clover with time, and some favorable rainfall seasons (data not shown). Soil organic matter increased as pasture productivity improved, and this, in turn, increased nutrient cycling and hence nutrient availability in the model. Phosphate availability was the key factor governing the productivity of the whole grazing system because phosphorus limitations to subterranean clover growth also limited the acquisition of nitrogen via nitrogen fixation.
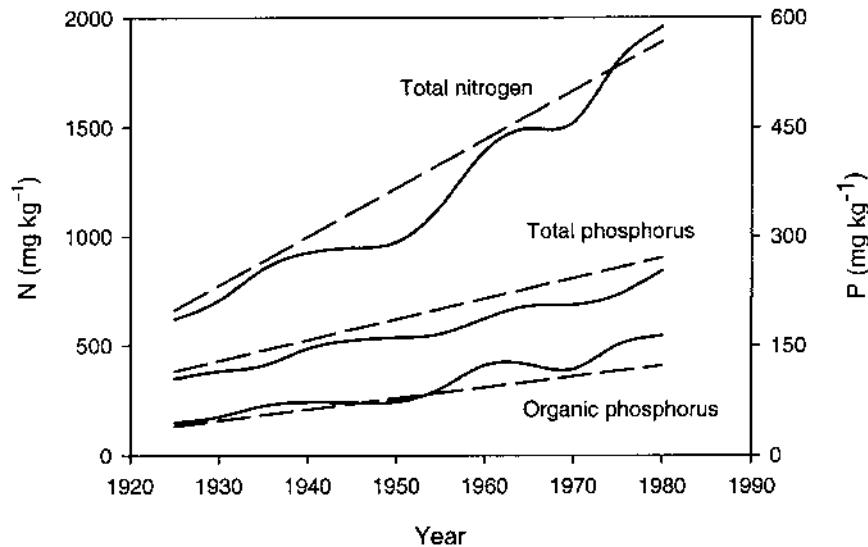
FIGURE 10 Total nitrogen, total phosphorus, and organic phosphorus contents in the 0 to 10 cm layer of the soil. Broken lines represent regressions fitted to measured data published by Williams [99]. Solid lines represent simulation results.

6.4 Relative Contribution of Different Processes to the Acid Budget

Knowledge of the sources of acid generation and the flow of protons within the system is important for understanding the underlying mechanisms. The contributions of the different carbon cycle and nitrogen cycle terms in the simulation are listed in Table 4 alongside previous estimates by Helyar and Porter [4] for the same site.

The GRAZPLAN soil acidity model calculated a total acidification rate of 3.38 kmol H^+ ha^{-1} $year^{-1}$ in this simulation. Helyar and Porter [4] estimated the acidification rate to be 3.46 kmol H^+ ha^{-1} $year^{-1}$ using the pH change between 1925 and 1980 and the pH buffer capacity in 1980 given in Bromfield et al. [21]. However, both values might underestimate the acidification rates. In the simulation, the decrease of the topsoil pH was not as great as the measured pH change (Fig. 11). Bromfield et al. [21] sampled to only 60 cm, and the estimate by Helyar and Porter [4] was based on that soil depth, but an examination of the soil pH pro-

TABLE 4 Total Soil Acidification and Sources of Acid or Alkali for a Grazed Pasture System on a Yellow Duplex Soil Developed from Granite (Units kmol H^+ ha^{-1})

Acidification component[a]	Estimates by Helyar and Porter [4]			GRAZPLAN simulation		
	55 years	Annual rate	% of total	55 years	Annual rate	% of total
Nitrogen cycle terms						
NH_{4ad}^+	0	0	0	0	0	0
NO_{3ad}^-	0	0	0	0	0	0
NH_{4ac}^+	−1.26	−0.02	−0.6	−5.09	−0.09	−2.7
NO_{3ac}^-	3.24	0.06	1.7	0.39	0.01	0.2
NH_{4ex}^+	0	0	0	0	0	0
NO_{3ex}^-	76.9	1.4	40	40.6	0.74	21.8
Carbon cycle terms						
OA_{ax}	81.8	1.49	43	118.58	2.16	63.8
OA_{ex}	28.3	0.52	15	33.82	0.61	18.2
OA_{ad}	0	0	0	−1.47	−0.03	−0.8
Mass flow (H^+, OH^-, HCO_3^-)	2.0	0.036	1	−0.85	0.016	−0.5
Total acidification	191	3.46[b]	100	186.00	3.38[c]	100

[a] For explanations of the individual acidification components see Eq. (1).
[b] Based on measurements of Bromfield et al. [21].
[c] Based on a dynamic simulation of the production system using daily time steps over 55 years.
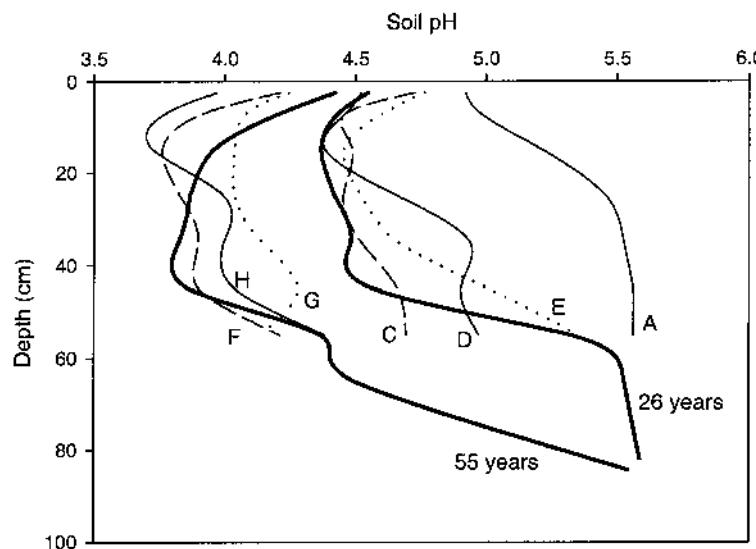
FIGURE 11 Soil pH profiles under subterranean clover–based pasture on granite-derived, yellow duplex soils. Measured values are shown as fine lines. Profile A, the average of values presented for "virgin soil" profiles A and B by Bromfield et al. [21]. It was used to initialize the simulation in January 1925. Profiles C, D, and E, 26-year-old pastures; F, G, and H, 55-year-old pastures [21]. Simulated values are shown using thick solid lines: after 26 years (January 1951) and after 55 years (January 1980).

files indicated that the soil had acidified below that sampling depth. This implied that the acidification rate was probably higher than the values given in Table 4. Although the estimates of total acidification produced by the simulation were consistent with the calculations of Helyar and Porter [4], the proportionate effects of carbon cycle and nitrogen cycle terms were different. Helyar and Porter [4] attributed 59% of the total acidification to the carbon cycle and 41% to the nitrogen cycle, whereas in the simulation reported here the relative contributions were 81% and 19% respectively. Without measured data for soil carbon or nitrate leaching at this site, the relative proportion of the carbon and nitrogen cycles to acidification there remains uncertain, as discussed in the following.

In the simulation reported here, the carbon cycle was the most important contributor to the acidification rate. The organic anion accumulation, the major carbon cycle term, accounted for 2.16 kmol H^+ ha^{-1} $year^{-1}$ or 64% of the total acidification. In contrast, Helyar and Porter [4] estimated the organic anion accumulation to be 1.49 kmol H^+ ha^{-1} $year^{-1}$, which was equal to 43% of the total acidification. However, this remains an area of uncertainty because the original

values for the soil organic carbon contents of this particular site were unknown and were estimated independently in the two studies using different procedures.

The organic anion export, which comprises organic anions removed in animal products, transported to sheep campsites, and deposited there in dung and urine, was predicted to result in 0.61 kmol H^+ ha^{-1} $year^{-1}$ in the simulation. This explained 18.2% of the total acid budget. In comparison, Helyar and Porter [4] assumed a lower stocking rate in their study and consequently the corresponding estimates were smaller: 0.52 kmol H^+ ha^{-1} $year^{-1}$ and 15% of the total acid budget. In the simulation here, it was assumed that the animals obtained extra supplementary feeding when necessary. The resulting organic anions added would have consumed 0.03 kmol H^+ ha^{-1} $year^{-1}$. Helyar and Porter [4] estimated the net changes due to mass flow of H^+, OH^-, and HCO_3^- to be acidifying, adding 0.036 kmol H^+ ha^{-1} $year^{-1}$ to the acid budget. In contrast, the simulation resulted in a small negative net mass flow (H^+, OH^-, and HCO_3^-) term of -0.016 kmol H^+ ha^{-1} $year^{-1}$. This can be explained by leaching of hydrogen ions out of the system. In the model, hydrogen ions can move considerable distances downward in short periods of time in major leaching events. It appears that this accounts for the small differences in the mass flow term.

The effects of nitrate and ammonium accumulation in the soil profiles on the acidification rate were small. However, the contribution of the nitrate leaching term (NO_{3ex}) to the acidification process was very important. In the simulation, 10.3 kg NO_3^--N ha^{-1} $year^{-1}$ was leached beyond the root zone, which equals an acid addition of 0.74 kmol H^+ ha^{-1} $year^{-1}$. Nitrate leaching was calculated from the simulated nitrate concentration and amount of drainage and was favored in years when the clover content of the pasture was high. Nitrate leaching in the simulation was episodic, occurring when the soil profile was saturated and rainfall high. Deposition of high concentrations of urea in urine patches was the key process contributing to nitrate leaching. When the simulation was run without urine patches (i.e., urine was distributed evenly over the whole paddock), very little nitrate was leached below the root zone. In the urine patches, nitrogen inputs exceeded nitrogen uptake by plants and opportunities for nitrate leaching occurred. This is consistent with the report by Ridley et al. [16], where fertilizer nitrogen was applied at rates that are likely to be deposited in urine patches, and nitrate leaching under annual ryegrass pasture was 11, 314, and 32 kg N ha^{-1} in three consecutive seasons in the nitrogen-fertilized plots compared with 7, 19, and 21 kg N ha^{-1} in the control plots. At the moment, our modeling of urine patches is rudimentary. We need to know more about the seasonal livestock water balance and the consequences for patch size, the areas in paddocks that are affected by urine, the duration of patch nitrogen influences, leaching of urea within patches, and the transient soil pH changes that occur [101]. These factors influence the nitrogen concentration of the affected soil, the rate at which nitrification proceeds, and, ultimately, the likelihood that nitrate will be leached.

At this stage of its development, the model does not simulate nutrient transactions between sheep camps and the rest of the paddock. Net nutrient or alkalinity deposition in camps is treated as export from the paddock. Nitrate losses from camp areas could have added up to 8.4 kg N ha^{-1} $year^{-1}$ to the size of the nitrate-leaching term recorded for the simulations.

Helyar and Porter [4] estimated that nitrate leaching added 1.4 kmol H^+ ha^{-1} $year^{-1}$ to the soil acid budget, almost twice the rate given by the simulation. Helyar and Porter [4] determined the acidification due to nitrate leaching indirectly as the component of acid addition that could not otherwise be accounted for (i.e., the retrospective application of the model as discussed in the introduction to this chapter). Because the total acidification rate was determined by pH change and pH buffer capacity, the estimate of the nitrate leaching term by this method depends directly upon the estimates of the carbon cycle terms.

6.5   Soil pH Profile Development

Soil pH profiles measured by Bromfield et al. [21] as well as pH profiles simulated by the GRAZPLAN soil acidity model for 26 and 55 years are given in Fig. 11. In the first 26 years of the run, both the total acidification and the distribution of pH within the soil profile lie within the range of the measured pH profiles for 26-year-old pastures (Fig. 11, profiles C, D, and E). The simulated pH profile for 1980 should be most comparable to measured profile H because the pH buffer capacity, the depth of the A horizon, and other factors used in the simulation were derived from data for this profile. However, the ranges of pH values at each depth across all three profiles (F, G, and H) probably give a more realistic target for comparisons as they give some idea of the variance that might be expected in acidified soil profiles. Total acidification after 55 years was similar to that calculated from the measured pH profiles. The simulation gave a substantial decline in soil pH in all soil layers. However, the change in pH of the 0 to 30-cm layer was underestimated, whereas a large amount of protons went into the 60- to 70-cm soil layer. The balance between alkalizing and acidifying processes determines the net acid addition in each soil layer. The main acidifying processes are net proton excretion by the roots due to excess cation and ammonium uptake and proton generation due to nitrification of ammonium. Because the proton-generating processes in the nitrogen cycle are restricted to the upper soil layers and leaching of protons and aluminum is limited above pH 4, the distribution of the excess cation uptake effects is clearly a significant factor for the distribution of acidity in the subsoil layers. There is no clear experimental basis—in either the field or laboratory—for modeling the distribution of excess cation uptake across a root system, so a number of alternative strategies were explored (data not shown). For instance, excess cation uptake was distributed according to the distribution of nitrate uptake, the distribution of root mass, or the distribution of root tips. All failed to reproduce the observed soil pH profiles. The best solution was to distribute the hy-

drogen ion excretion due to excess cation uptake according to the distribution of root mass but modified by dependence on soil pH as described earlier. This has produced sensible results in a situation where the subsoil has acidified strongly. However, the restriction on excess cation uptake needed to obtain a reasonable pH distribution was greater than would be expected from the physiology of cation uptake alone [50]. We presume that there is not only a physiological effect of pH on excess cation uptake but in addition poor availability of cations [102] and toxic effects on root and root hair development in the acid soil layers [103]. The current logic of distributing proton excretion due to excess cation uptake provides an interim solution, and further work is required.

6.6 Conclusions: GRAZPLAN

Modeling of soil acidification under extensive grazing is particularly challenging because the phosphorus input drives carbon and nitrogen cycle acidification through several intermediate steps, e.g., nitrogen fixation by clover and nutrient redistribution by the grazing animals. Nevertheless, the GRAZPLAN soil acidity model was used successfully to simulate the impact of subterranean clover–based pasture on the soil pH profile development over a period of 55 years.

The work has identified areas where new knowledge is required for further progress in simulation of soil acidity. In particular, we are examining aspects of phosphate sorption, phosphate fixation, plant availability of phosphorus, and soil organic matter turnover in relation to plant productivity. In the present simulation, these factors were controlled. For instance, the phosphate sorption characteristic of the soil was set on the basis of results from a grazed fertilizer trial in progress on a similar soil, while rates of soil organic matter turnover were set to mimic the accumulation of organic nitrogen and phosphorus reported by Williams [99]. This allowed us to concentrate on issues that affected the generation and distribution of soil acidity under a pasture system. Simulation of the pH profile data reported by Bromfield et al. [21] revealed that two areas of the soil acidity model in particular require further examination: (1) the spatial distribution of excess cation uptake and proton excretion along root systems in soil and (2) the interaction with soil pH and the characteristics of urine deposits on grazed pastures and the associated nitrogen dynamics under urine patches. The interim solutions to both of these problems in the model have provided working hypotheses that will form the basis of further experiments. This case study shows that the integration of experimental and modeling approaches can be used synergistically to further our understanding of biological and chemical processes underlying agricultural systems.

7 CONCLUDING REMARKS

The implementation of the Helyar and Porter proton budget calculations in two agricultural systems models improves on the manual application of the framework

and presents more opportunities for analysis of soil acidification in agricultural systems. When properly parameterized, the two models described in this chapter are powerful tools for interpreting and extrapolating experimental data. As illustrated in the APSIM-SoilpH case study, use of the model for extrapolations in time can put the results and conditions of a short-term experimental study in perspective. When considering, for example, the amount of nitrate leaching measured in a single year, it goes beyond a simple comparison of seasonal rainfall with the long-term average by giving an integrative analysis of the effect of timing of rainfall relative to nitrogen uptake by the crop and management actions such as fertilization. Similarly, in the second case study the GRAZPLAN soil acidity model allows an analysis of processes occurring between experimental sampling dates, such as the nonlinear increase in total soil nitrogen.

Although the simulations presented in the case studies do not allow complete verification of all aspects of the models' performance, they give sufficient confidence that the models describe the key proton-producing and proton-consuming processes well and are able to describe the pH profile development over time. In preparing the case study examples, we found, however, that accurate description of carbon and nitrogen dynamics is much more critical for modeling soil acidification than for simulating crop production or simulating drainage and nitrate leaching below the root zone. Some processes are currently not well defined due to lack of detailed experimental data, e.g., surface residue breakdown, below-ground fresh organic matter inputs (amount and C/N ratio of roots), and nutrient redistribution by grazing animals. Obviously, more work in these areas is required, preferably through well-defined experiments in conjunction with model development to ensure that the right data are collected.

This study stresses that the models are only as good as the science underpinning them and the inputs provided. How critical uncertainties about the process and input are generally depends on the type of application. Requirements for a qualitative "what-if" analysis are much less stringent than for a quantitative simulation of site-specific conditions.

Two types of model applications that are likely to become more and more important in the years ahead are not illustrated here, namely the use of models in the design of sustainable agricultural production systems and the use of models to support environmentally responsible and economically viable management decisions. Both APSIM-SoilpH and the GRAZPLAN soil acidity model provide opportunities in this area to analyze options for amelioration of soil acidity and to assist in management that will minimize soil acidification.

ACKNOWLEDGMENTS

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7

Using Geographic Information Systems (GISs) in Soil Acidification Risk Assessments

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1   INTRODUCTION

Risk is the probability that a hazard will become a problem [1]. In risk assessment, it is usual for risk criteria to be formally identified (e.g., Bui et al. [1]). First, it is necessary to determine what hazards contribute to the risk of the problem occurring. Second, criteria that need to be evaluated in order to determine the risk have to be established. Finally, it is necessary to ascertain at what level the hazard will become a problem.

The factors that contribute to the hazard of soil acidification include the initial soil pH, the soil pH buffering capacity, and the acidification rate [2]. Equation (1) can be used to estimate the number of years required for a soil to reach a critical pH value below which production losses are likely [2].

$$\text{Time} = \frac{(\text{pH} - \text{pH}_{\text{crit}}) \times (\text{pH B.C.})}{\text{A.R.}} \qquad (1)$$

where

time = the number of years it will take for the soil to reach the critical pH

pH = the current pH of the soil measured in 1:5 soil/0.01 M $CaCl_2$
pH B.C. = the buffer capacity of the soil in kg lime (ha^{-1} 10-cm depth) $year^{-1}$
A.R. = the acidification rate in kg lime (ha^{-1} 10-cm depth) $year^{-1}$
pH_{crit} = the critical pH_{CaCl2} below which production losses are likely

In soil acidification risk assessments, as with most agricultural risk assessments, a "problem" occurs when productivity, or the sustainability of productivity, is affected. This happens when soil pH drops below a critical pH level. Identifying areas that are at high risk of soil acidification is achieved through determining the number of years until critical pH is reached, given the value of each of the contributing risk factors at any geographic location within the study area.

2   ACIDIFICATION RISK ASSESSMENTS

The expected number of years until a given critical pH is reached enables acidification risk predictions to be made by identifying the bracket within which the number of years falls. For example, a high-risk area is expected to reach critical pH in less than 15 years, a moderate-risk area in less than 30, and a low-risk area is not expected to acidify to critical pH within 30 years [3]. Where enough data are available, it is possible for maps to be created to represent the categories spatially [2].

Unlike assessment of acid sulfate soils [4] and salinization risks [1], it is not possible to use remotely sensed data to infer geomorphic features that are generally associated with areas with high risk of acidification using digital elevation models. The factors that contribute to agriculturally significant soil acidification are necessarily measured using soil surveys. Hence, soil surveys will always form a part of soil acidification risk assessments.

2.1   Initial Soil pH and Critical Soil pH

Management of acid agricultural soils involves increasing the soil pH to the point where economically significant decreases in plant production are avoided, usually within the economically significant pH range of 4 to 7 where soils are less well buffered [5,6]. Acidification forecasts and predictions of lime application requirement are also restricted to this range because alkaline soils are affected minimally as a result of strong buffering by carbonates and acid soils by the buffering of aluminum hydrous oxides [7].

The Al^{3+} ion is a major constituent of mineral soils, where it is present in a wide array of primary and secondary minerals [8]. It is generally considered to be the main aluminum ion that is toxic to plants, and it increases in concentration in soil solution below pH 5.5 [8–10]. Aluminum concentrations in soil that have been shown to affect plant growth vary according to plant susceptibility; critical

pH values have been determined for categories of susceptibility of plant species to Al toxicity [11–13].

2.2 Acidification Rate

In simulating future soil acidification, it is necessary to determine the acidification rate, which is a factor of net acid addition to, and loss of alkalinity from, the soil system. Acidification rates are related to land use, and increases in acidification rates compared with undisturbed systems are a characteristic of southern Australian agricultural systems [14]. Determining current acidification rates is imperative for facilitation of corrective action because prolonged periods of high acidification rates may result in subsoil acidification. Ameliorating subsoil acidification is not always economically viable [14].

Acidification rates have been determined historically from the change in pH over a given time period [Eq. (2)] [15,16]. This may be done for the same site over time or for adjacent sites with different land uses (fenceline surveys) [14].

$$\text{Acidification rate} = \frac{\Delta \text{pH}}{\text{year} \times (\text{pH B.C.})} \tag{2}$$

Acid addition rates are related to the production system, fertilizer and acid inputs, soil texture, organic matter content (pH buffering capacity), time since clearing, annual rainfall, and initial pH [14,15,17].

Time since clearing has been shown to influence the acidification rate, with rates observed ranging from -0.39 kmol H^+ ha^{-1} per year for 8 years from clearing to 1.58 kmol H^+ ha^{-1} per year 40 years from clearing [18]. Dolling and Porter [19] reported similar observations, with acidification rates from 0.19 to 0.23 kmol H^+ ha^{-1} per year from 12 to 74 years since clearing.

The average annual rainfall determines crop yields and hence removal of alkaline plant produce from the paddock, as well as the degree to which nitrate is leached. For example, acidification rates under continuous wheat rotations are directly related to rainfall [20]. Also, leguminous crops produce greater soil acidification rates than cereal crops [21].

2.3 Buffer Capacity

The buffer capacity of soils refers to the impact that addition of either acid or base has on the soil pH; i.e., the buffer capacity is the in situ titration curve of the soil [5,22]. Soil pH buffer capacity can be measured in the laboratory [22,23]; however, it is rarely measured for soils because of practical problems associated with buffer capacity analyses on a large scale. Buffer capacity may also be predicted from other soil properties that are readily measured or observed, such as organic matter and clay content [17,24,25]. Equations involving both organic carbon and clay content have been used in Queensland [17] and Western Australia [14].

Clay has been shown to have a weak buffer capacity relative to organic matter [26]. In fact, the buffering contribution of organic matter may be in the order of 10 times that of clay. Values for organic matter have been reported as being between 4 and 10 kmol H^+ ha^{-1} per pH unit and per 10 g organic matter kg^{-1} soil and clay buffer capacity as being between 0.45 and 0.62 kmol H^+ ha^{-1} per pH unit and per % clay [5]. Helyar et al. [14] state that for Australian soils values of 4.2 kmol H^+ ha^{-1} per pH unit or 10 g organic matter kg^{-1} soil and 2 kmol H^+ ha^{-1} per pH unit and per % clay should be used. Simple equations have been determined that relate buffer capacity to organic matter based on the assumption that all organic matter has an equal buffer capacity and that there is enough organic matter to influence strongly the soil buffer capacity [3].

Curtin and Rostad [26] concluded that in situations where clays are weakly buffered due to mineralogy (e.g., kaolin-dominated clay) and where organic matter is low, soils would be susceptible to acidification even when clay content is relatively high. As significant differences in pH buffer capacity between soil groups have been observed [17], it is likely that buffer capacity calculations based on soil properties will be region specific.

In Western Australia, regional mapping has shown the existence of a generally uniform pattern of soils and landforms, referred to as a catena or toposequence [27]. Local geology and soil formation determine soil characteristics, in particular clay mineralogy and soil texture, that in part determine the buffer capacity of the soil. Hence, it seems reasonable to expect to be able to predict the comparative buffer capacities of disparate soils within a region. The buffer capacity may also be inferred from the relationship between landform and soil texture for any given region; e.g., soils on ridges may be associated with a buffer capacity different from that of soils that are found on slopes.

3 GEOGRAPHIC INFORMATION SYSTEMS

The ability of a geographic information system (GIS) to handle geographic data in digital form enables diverse sets of spatial data to be captured, stored, manipulated, analyzed, and finally displayed [28]. There are two main data structures in GISs. Vector structures use points, lines, and polygons to represent the location and extent of features such as sample sites (points), fencelines (lines), and land use (polygons). Raster structures use a regular grid for which each cell has a value for any geographic variable, for example, soil clay content or pH.

Soil maps frequently form a component of spatial analyses related to agriculture. In particular, the development of precision agriculture has seen the associated evolution of GISs and methodology capable of producing soil maps with some accuracy. The importance of soil mapping is derived from the fact that soil properties control a range of processes that have significant consequences for agricultural and environmental management [29].

The final soil maps produced have historically relied on the ability of the soil surveyor to infer features of soil variation from readily observable attributes [29]. This process is based on the assumption that development of soil characteristics is reliant on five principal soil-forming factors and processes, these being parent material, landform, time, climate, and biological activity [30]. On the other hand, the soil map may be created within the GIS environment using a raster data structure; this method relies less on user interpretation than on mathematical relationships [31]. The best method for producing a soil map is one that uses conceptual models devised by a soil scientist and is complemented by the objectivity of GIS.

Cook et al. [29] introduced a rule-based approach to mapping soil properties. Prediction of an unquantified soil characteristic at point x is made according to the value of other quantified characteristics that are known to influence the unquantified characteristic [29]. As discussed previously, it has been shown that clay and organic matter contents are determinants of soil buffer capacity. Hence, knowing the value of the predictor variables (in this example clay and organic matter contents), we are able to make some assumptions about the unquantified characteristic, in this case the buffer capacity, at any unvisited site.

This method is further developed by weighting the evidence according to its perceived sufficiency or necessity [29]. It was shown earlier that the buffer capacity for any given point x may be estimated on the basis of organic matter content and clay content. Weighting the influencing characteristics according to a tested equation can provide accurate predictions about the value of the buffer capacity at an untested site using values of characteristics that are readily observed. That is, buffer capacity may be spatially estimated using an experimentally determined equation.

3.1 Spatial Interpolation of Soil Properties

Representation of spatial continuity is possible by depicting the surface continuously to show gradual variations in soil properties [32]. This may be achieved by interpolating values of variables at unvisited sites in the GIS on a cell-by-cell basis in a raster environment.

The resultant map using interpolation is considered accurate compared with conventional chloropleth maps in some situations. For example, Burrough [33] showed that mapping the clay content of the topsoil for an area in Italy using conventional mapping gave an average 39% variance for clay content. Using interpolation produced a map for which the error variances did not exceed 21% clay content, which in effect was 2.5 times better than the chloropleth map [33].

Powell and Ahern [4] have delineated risk factors using a vector data structure in assessing the risk of acid sulfate soils. Moore [2] has also developed a method of producing soil acidification risk maps using GISs in which an acidification risk value was associated with each soil type, producing risk maps that

showed discrete (and hence artificial) boundaries. This problem has been overcome by interpolating the soil properties that are shown to affect soil acidification risk, resulting in continuous surfaces that more closely represent reality [34]. The following steps are applied to a data set in order to produce continuous soil acidification risk maps:

1. Development of a soils map and association of the various soil types with bulk density values
2. Acquisition of point observations of soil pH, organic matter, exchangeable aluminum content, clay content, and buffer capacity
3. Determination of a relationship between soil buffer capacity and the other soil properties
4. Interpolation of grids of the factors in step 2 that were used in step 3 and a grid of initial pH
5. Use of raster algorithms to weight the various factors according to the relationship in step 3
6. Incorporation of the initial pH grid with the buffer capacity to produce acidification risk maps and lime requirement maps [34]

4   A CASE STUDY—THE WEST RIVER CATCHMENT*

4.1   Study Area

The West River Catchment is 43 km west of Ravensthorpe, 30 km from the south coast of Western Australia, and covers approximately 30,000 hectares (Fig. 1). The area receives an average rainfall of 370 mm at the north of the catchment and 420 mm to the south [35]. The main produce of the area includes wheat, barley, lupins, canola, sheep, and cattle.

The West River joins the Phillips River within the Fitzgerald River National Park, and the Phillips River drains into the Southern Ocean 20 km west of Hopetoun. The catchment is separated from the ancient internal drainage lines and salt lake chains by the Jarrahwood axis [36]. The catchment consists of a shallow, narrow valley, 15 km wide, with the highest point of the catchment being 350 m above sea level and the lowest 240 m above sea level.

The higher regions of the catchment are mainly colluvium derived from granitoid rocks including granitoid gneiss; the flats are undulating, reworked sandplain deposits and peneplain remnants. Drainage lines contain silcretes formed in regolith over granitoid rock, with some biotite monzogranite and granodiorite coinciding with the river [37]. Influencing the soil pattern across the landscape are the full laterite profiles that may be observed in a transect from the higher regions into

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* From Hill [34].
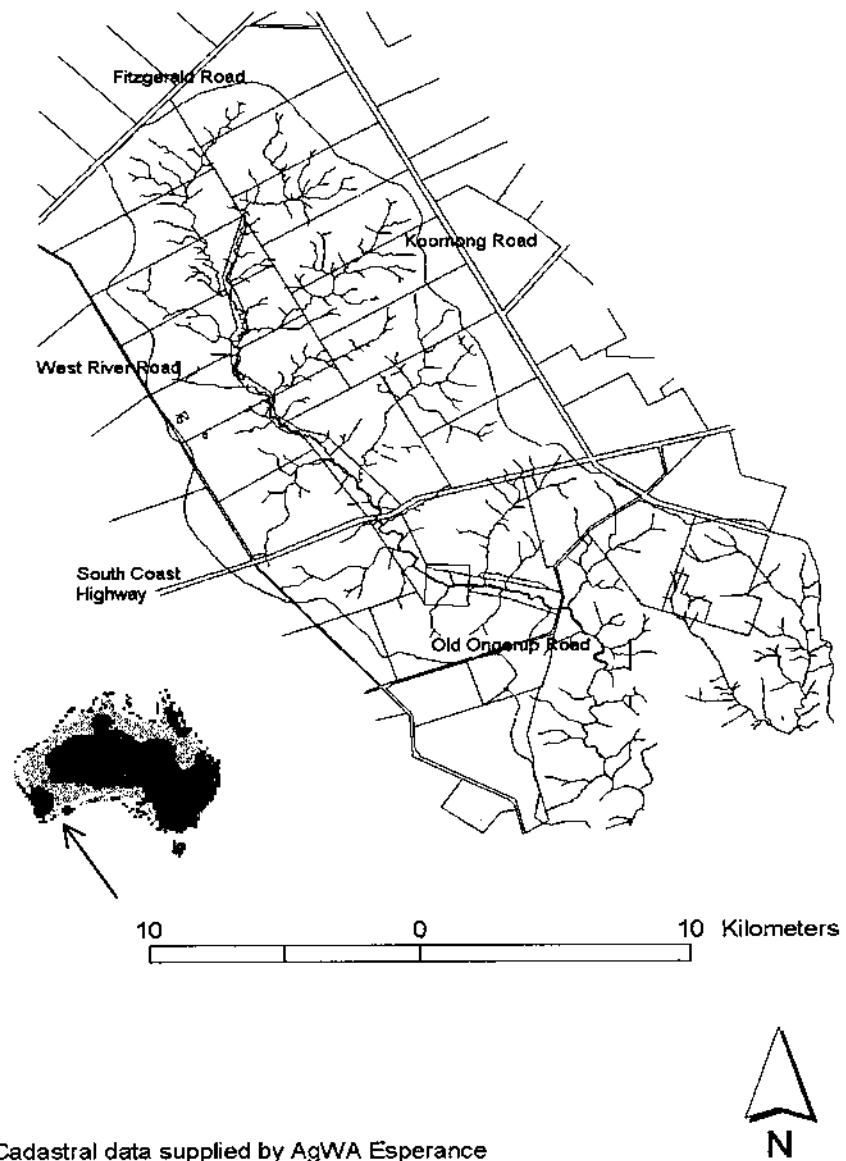
FIGURE 1   Location of the West River Catchment, Western Australia.

the drainage lines. Laterite breakaways of the peneplain are actively eroding [35]. Short et al. [35] observed that the present soils have formed primarily on the pallid zone clays, hence resulting in primarily duplex soils. It is also noted that there are many dolerite dykes throughout the southern part of the catchment.

4.2 Collection of Case Study Data

A soil survey was conducted in April 1999 in order to collect soil samples from as many disparate soil types as possible. Sites were visited according to their land-form, delineated on the basis of predetermined soil mapping units using aerial pho-tographs. Actual location was determined using global positioning system (GPS).

From each site, topsoil and subsoil samples were taken from the profiles. Soil samples were analyzed for color, pH, extractable aluminum, soil pH buffer-ing capacity, texture (clay content), gravel content, and organic matter. Loamy sand accounted for 53% of the total area in the topsoil, while 75% of the subsoil was clay or sandy clay. Upland (plateau) soils were characterized by shallow and sandy gravels or sand over a gravel/loam matrix. Slope soils were generally du-plex soils, characterized by light-colored (gray) sands over gray or brown clays.

4.3 Initial and Critical Soil pH

Fifty-three percent of samples fell between pH 4.5 and 5.5. A significant system-atic relationship between the extractable aluminum and pH was observed [Eq. (3); Fig. 2).
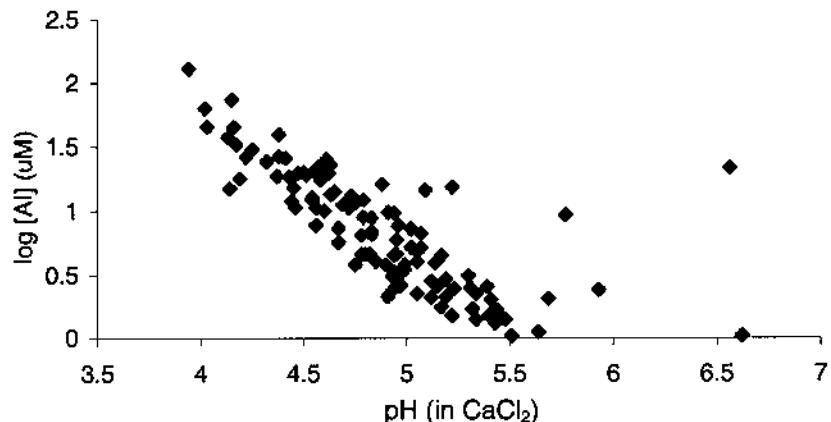
FIGURE 2   Relationship between the logarithm of $CaCl_2$-extractable aluminum and pH in 0.01 M $CaCl_2$ for 120 soil samples taken from the topsoil and the subsoil of profiles in the West River Catchment.

$$\text{Log [Al] (}\mu\text{M)} = -0.826(\text{pH}_{\text{CaCl2}}) + 4.87 \qquad R^2 = 0.73 \qquad (3)$$

Critical pH values were chosen on the basis of this relationship.

4.4 Buffer Capacity

Average carbon content for topsoil was 14 g kg^{-1}, 3.5 times higher than in the subsoil (4 g kg^{-1}). Both values are considered to be medium for their respective depths [38] (Fig. 3). For the average "fines" (<2 mm particle size), buffer capacity was 0.73 cmol H$^+$ kg^{-1} soil per pH unit (207 kmol H$^+$ per ha and per pH unit using bulk density values).

The factors found to contribute to buffer capacity predictions included the clay proportion and the organic matter content; however, the best relationships were obtained when the topsoil samples were separated from subsoil samples. The prediction of buffer capacity for the <2 mm fraction of the topsoil was significantly related to both the organic matter content and the clay content [Eq. (4)]

$$\text{pH B.C.} = 0.131 + 0.0161(\% \text{ clay})$$

$$+ 0.394\left(\frac{\text{g organic carbon per kg soil}}{10}\right) \qquad R^2 = 0.86 \qquad (4)$$

The buffer capacity for the subsoil was best predicted taking into account only the proportion of clay [Eq. (5)].

$$\text{pH B.C.} = 0.39 - 0.021(\% \text{ clay}) + 0.00091(\% \text{ clay})^2 \qquad R^2 = 0.97 \quad (5)$$
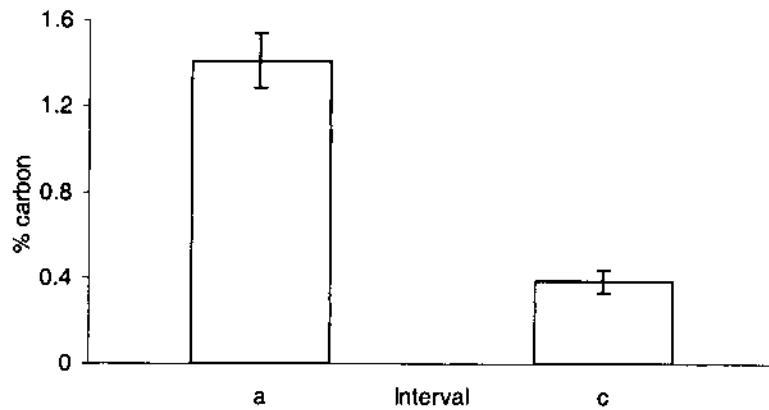
FIGURE 3 Average carbon content for the topsoil and the subsoil of profiles in the West River Catchment. Values shown are means $\pm$ standard error.

5 APPLICATION OF GIS TO THE CASE STUDY DATA

The spatial analysis was conducted using ARC/INFO, version 7.1.3 (ESRI). All steps were written into Arc Macro Language applications (AMLs) so that the process was fully automated. The AMLs were linked to a graphic user interface menu bar, allowing simple completion of simulations.

5.1 pH Data

The GPS coordinates of sites visited were associated with the corresponding pH data in tables in ArcView (ESRI). The entries for each separate depth (topsoil and subsoil) were selected from all entries in tables in ARC/INFO and were used to create coverages for each depth. These coverages were then used to create an interpolated pH grid for each depth using inverse distance weighting (IDW) in GRID.

5.2 Buffer Capacity

Several steps were required in order to create the buffer capacity grids for the topsoil and subsoil across the catchment.

1. *Determination of the predictors for buffer capacity:* the relationship between buffer capacity and other soil factors, as given previously [Eqs. (4) and (5)].
2. *Clay content:* interpolation of a clay grid using the point texture values was used to determine the clay content across the catchment. This was chosen in preference to creating a soil texture map and converting it into a grid because soil texture boundaries are an arbitrary delineation of a continuous surface, which could not be taken into account using the discrete delineation of polygons. An item "clay" was added to each depth's polygon attribute table (PAT) and was given a value according to the soil texture (derived from Needham et al. [39]). The clay point coverage was then interpolated into a grid using IDW in GRID. This allowed continuous representation of the surface so that further grids could be calculated using raster algorithms.
3. *Gravel grid:* a gravel grid was created from the "gravel" item in each depth coverage PAT, using IDW with the same cell size and map extent as for the previous grid.
4. *Carbon grid:* a carbon grid was created for the topsoil. An item "carbon" was added to the topsoil PAT and given a value according to the average value for the land use at that site. This item was then converted into a grid.
5. *Fines buffer capacity grid:* a buffer capacity grid was created for the <2 mm fraction ("fines") of the soil in each depth (topsoil and subsoil).

Equation (4) was used to create the fines buffer capacity grid for the topsoil and Eq. (5) for the subsoil.

6. *Total buffer capacity grid:* the total buffer capacity grid was then determined using Eq. (6a) [in terms of raster algorithms, Eq. (6b)], which gave the buffer capacity in cmol H^+ kg^{-1} soil (pH unit)$^{-1}$.

$$pH\ B.C._{Total} = \{[B.C._{Gravel} \times (\%\ gravel)]$$
$$+ [B.C._{fines} \times (\%\ fines)]\} \tag{6a}$$

$$totbuff = [0.144 \times (intgrav/100)]$$
$$+ [finebuff \times (1\text{-}intgrav/100)] \tag{6b}$$

In Eq. (6a), total buffer capacity (B.C.$_{Total}$) is determined by proportion of gravel multiplied by its buffer capacity in cmol H^+ kg^{-1} soil (pH unit)$^{-1}$ (B.C.$_{Gravel}$) plus the <2 mm fraction multiplied by the fines buffer capacity value (B.C.$_{fines}$). In Eq. (6b), Eq. (6a) is converted into a raster algorithm, where totbuff is the total buffer capacity created, intgrav is the interpolated gravel grid, finebuff is the fines buffer capacity grid, and 0.144 is the observed average buffer capacity of ferruginous gravel in cmol H^+ kg^{-1} soil (pH unit)$^{-1}$.

7. *Conversion of buffer capacity grid:* a total buffer capacity grid was created in units of kg lime ha^{-1} (pH unit)$^{-1}$ so that acidification risk and lime requirements could be calculated. An item BD (bulk density) was added to the texture coverage PAT and given values in t m^{-3} on the basis of those given in Needham et al. [39]. The texture polygon coverages were then converted into grids using the BD item.

Buffer capacity values were converted to kmol H^+ (ha^{-1} 10-cm layer) (pH unit)$^{-1}$ using the conversion equation of Moore et al. [3] [Eq. (7a)], where pH B.C. is the soil pH buffer capacity and BD is the bulk density grid. Conversion into a raster algorithm gives Eq. (7b).

pH B.C.$_{(kg\ lime\ per\ ha\ 10\text{-}cm\ layer\ per\ pH\ unit)}$

$$= pH\ B.C._{(cmol\ H+\ per\ kg\ soil\ per\ pH\ unit)} \times \frac{500}{BD} \tag{7a}$$

$$B.C._{converted} = \left[\left(\frac{\%\ gravel}{100}\right)(B.C._{gravel})\right]$$
$$+ \left[\left(1 - \frac{\%\ gravel}{100}\right)B.C._{fines}\right]\left(\frac{500}{BD}\right) \tag{7b}$$

where the total buffer capacity grid in kg lime ha^{-1} (pH unit)$^{-1}$ (B.C.$_{converted}$) is created using the gravel grid (% gravel), the gravel buffer capacity (B.C.$_{gravel}$ =

0.144), the fines buffer capacity (B.C.$_{fines}$, in cmol H^+ kg^{-1} soil (pH unit)$^{-1}$, and the bulk density grid (BD).

The processes just described are summarized in Fig. 4.

Buffer capacity of surface soil is generally uniform across the catchment, being between 200 and 400 kg lime ha^{-1} (pH unit)$^{-1}$. The subsoil shows more variation in buffer capacity, with most of the east side of the catchment having a buffer capacity between 100 and 300 kg lime ha^{-1} (pH unit)$^{-1}$ and the west side between 0 and 200 kg lime ha^{-1} (pH unit)$^{-1}$.

5.3 Years Until Critical pH Is Expected to Be Reached

The predicted number of years until critical pH is expected to be reached was determined using Eq. (1) [3]. Acidification rates were chosen from the data pre-
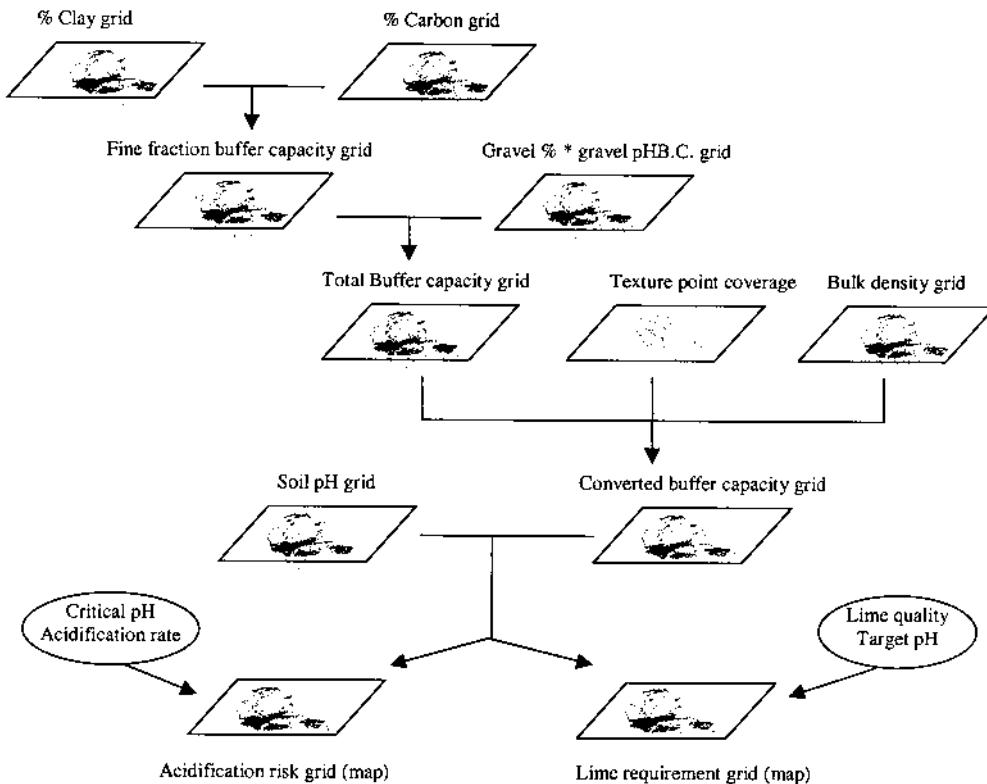
FIGURE 4 Summary of processes undertaken to produce acidification risk assessments using geographic information systems.

sented in the literature. These values were converted into kg lime ha^{-1} year^{-1} so that they could be used in Eq. (1). This was achieved using the assumption that 1 mole of CaCO$_3$ neutralizes 2 moles of H$^+$ in the soil (G. Moore, personal communication, 1999).

Maps of the number of years until critical pH is expected to be reached were created for critical pH values of 4.05, 4.13, and 4.55. These values correspond to the pH at which extractable soil aluminum reaches critical concentration for tolerant ([Al] = 45 μM), sensitive ([Al] = 37 μM), and highly sensitive ([Al] = 15 μM) plants, respectively, based on the relationship shown in Fig. 2. Acidification rate values were chosen to cover a wide range of acidification rates from the literature, including 2, 4, 7, 10, and 20 kg lime ha^{-1} year^{-1} (this refers to the lime equivalent removed from the soil system for the 10-cm layer, dependent on crop type).

5.4 Acidification Risk

Acidification risk grids were created using several of the "years until critical" grids (created as described earlier). In this way, risk grids could be created for any given scenario determined in the years until critical component. Each raster cell of the grid was given a value according to the years required to reach the critical soil pH value for each raster cell of the critical grid. Cells with a value of 3 or less were given an acidification risk value of 1 (imminent risk), cells with a value between 3 and 15 were given an acidification risk of 2 (high risk), cells with a value between 15 and 30 were given a value of 3 (moderate risk), and above 30, cells were given a risk value of 4 (low risk).

The acidification risk maps show that for the topsoil, there are three areas that are at the highest risk of acidification. These areas are along the highway, at the southeast of the catchment, and a small area along the northern boundary of the catchment. For the subsoil, the high-risk areas are scattered throughout the catchment but trend north–south through the center of the catchment (Fig. 1).

6 USING GIS IN ACIDIFICATION RISK ASSESSMENT— ADVANTAGES AND DISADVANTAGES

Due to the degree of erosion of the West River Catchment, the clay minerals, derived from granitoid rock and granitoid gneiss, are likely to be highly weathered [37]. It is therefore assumed that, like most soil clays in Western Australia, the clays in West River soils are predominantly kaolinitic (T. Overheu, personal communication, 1999) [40]. Because kaolinitic clays have low cation exchange capacity compared with other clays and consequently a relatively low buffer capacity [41], most of the catchment is at high risk of soil acidification.

Ascertaining the nature of the soil catena across the landscape can allow general statements to be made about the acidification risk of a region. In particu-

lar, soils formed on lateritic profiles are inherently low in bases [42] and high in kaolin and/or aluminum hydroxide [43]. This has significance for acidification studies due to the toxicity of aluminum at low pH. Furthermore, because buffering capacity was shown to be closely related to clay content, a conceptual framework may be established such that land managers may prioritize lime application to landforms known to possess a particular suite of acidification-susceptible soils.

Accuracy of soil acidification assessments is limited by the strength of the relationships used to predict the soil pH buffer capacity [23]. In the case study data, buffer capacity was predicted with a high degree of confidence. This may be attributed to a large sample size and geographically confined nature of the study—soils and land use were fairly uniform across the catchment.

Soil pH buffer capacity predictions are calculated from the rate of pH change with addition of acid or base in the range where the slope is greatest. This was determined as being between pH 4 and 6.5, with rate of pH change diminishing outside this range. Hence, predictions of pH change with the addition of lime or acid will be restricted to this range. Due to the high buffering of soils below pH 4 by aluminum hydrous oxides and kaolinite, it is unlikely that soil pH will decline much below 4 [7]. Predictions of pH decline will therefore be overestimated for soils with pH below 4, resulting in pH predictions for acid soils that are too low.

In contrast to findings by Curtin and Rostad [26], organic matter was shown to have a significant influence over buffer capacity only in the surface soil. On the other hand, including clay content improved the accuracy of the buffer capacity prediction equation for both the topsoil and the subsoil. Extractable aluminum has also been used to predict pH buffering capacity, e.g., in Queensland soils [44]; however, aluminum was not significantly related to buffering capacity in this study. This is probably because buffer capacity was measured between pH 4 and 6.5, where neutralization of exchangeable aluminum is not an important factor in buffering change in soil pH [14]. In this pH range, the main buffering reactions are proton dissociation and association from pH-dependent groups on the edges of clay minerals and oxides and from the carboxyl, hydroxyl, and phenolic groups of organic matter [14].

The dominant role of organic matter in soil buffering may be due to its high affinity for acidic metal cations [45]. Humic substances form relatively stable complexes with acidic cations, e.g., Al^{3+}, both in soil solution and adsorbed to the surface of clay minerals [45]. On addition of protons to the soil, organic matter plays a role in providing adsorption sites for fast reaction [25]. Organic matter source and degree of humification are thought to affect the buffer potential per unit mass of organic matter, and it is noted that surface organic matter was generally not highly decomposed, possibly influencing the number of reactive sites in the organic matter. Hence, although organic matter quantity is high in soil under cereal stubble, its quality may predicate that the buffer capacity for each unit of

organic matter is overestimated. The equation assumes that all organic matter has equal buffer capacity, which is unlikely.

Organic matter content in the subsoil was probably not sufficient to influence the buffer capacity. Also, inclusion of organic matter for the subsoil was not possible because there was no surrogate measure that could be interpolated to predict accurately organic matter content across the catchment. That is, unlike the topsoil, differences in organic matter content for each land use were not systematic. It is recommended that land managers acquire data on soil organic carbon content in order to determine the buffer capacity for topsoil.

The significant influence of clay is probably related to the high clay content in the subsoil and is despite the low chemical activity of kaolin group minerals. The average buffer capacity for the catchment is low compared with predicted buffer capacity values using the equations given in Moore et al. [3] and similar clay and organic matter content values. It is concluded that the clays in the West River catchment are poorly buffered against pH change, even though clay is the most significant source of active sites within the pH range 4 to 6.5.

The acidification risk equation used in the case study relies on the accuracy of soil pH buffering capacity and acidification rate values. The equation is simplistic, assuming that the in situ buffer capacity is equivalent to that observed in the laboratory. It also assumes that buffer capacity remains constant with time, which is unlikely because organic carbon contents are dynamic, increasing and decreasing in relation to land management practices. Predictions of acidification risk are therefore likely to be more accurate for the subsoil because clay content will remain relatively constant with time. Using a constant acidification rate also ignores the influence of variable rainfall and land use across the catchment. It is expected that land managers will use a value that best represents the acidification rate for their situation, based on published data. When more accurate acidification risk equations become available, they will be readily incorporated into the GIS.

Acidification rate data are scarce, particularly for the southern coastal area of Western Australia. Acidification rates are rarely determined for separate depths, and in the absence of such data and for the purpose of this study, the acidification rate values were chosen to cover a wide range. Obtaining data for the actual acidification rate for sites within the catchment may allow more appropriate values to be chosen because acidification rates are affected by soil properties, climate, land use, and land management practices [14,15,17].

The clear relationship between pH and extractable aluminium means that critical pH values, based on the pH at which aluminum reaches a critical concentration, may be determined with a high level of confidence. A good relationship between pH and extractable aluminum is expected in the absence of organic matter and low concentrations of inorganic compounds that adsorb aluminum [46]. This is further evidence that the clays and organic matter in the catchment are relatively unreactive, having few adsorption sites to either buffer against pH change

or adsorb aluminum. Choosing critical pH values on the basis of critical soil solution aluminum concentrations for plants ignores the effects on other factors, e.g., soil biological activity.

The acidification assessment is a time-consuming process; however, writing the separate processes into AMLs will mean that future assessments are expedited, and a similar soil acidification assessment could be completed in a very short period of time, depending on the scale of the study. The process also required a system capable of analyzing and storing very large files, so is probably not suited to small or inefficient computers. Also, the software used for this assessment (ARC/INFO) is a package that is not readily available to land managers. Aside from the computational requirement, the initial assessment relied on advanced GIS knowledge. However, linking the AMLs to a graphic user interface in the GIS environment will allow users with little or no GIS knowledge to perform an equivalent study.

Using inverse distance weighting was a means of interpolating the grids while returning the exact value at the sample sites. The resultant grids show maxima and minima in unrealistic spatial patterns, such that barriers to spatial spread are not taken into account. Also, IDW does not take into account spatial variability of the regionalized variable [47]. It may be possible to develop associations between soil mapping units and other characteristics within the GIS. This would enable the use of mapping units to act as barriers to the spatial spread of the variables and also ensure that only values obtained for the same mapping unit were considered when interpolating the surface. For example, averages of the clay buffer capacity would have been separated into the mapping unit from which the original observation was made—upper slope values would have been interpolated separately from lower slope values and so on. This would allow a more accurate interpolation procedure to be used (such as kriging) to give superior results in terms of accuracy compared with inverse distance weighting.

It was not possible to use kriging in this case because the distance between sample sites was above the maximum allowable for that procedure [48]. Kriging uses the dependence between spatially located observations represented by a variogram model and weighted according to the spatial dependence between observations [47]. In regions where the soil–landscape relationship is well defined, kriging will greatly improve the accuracy of soil acidification risk assessments. It is probably not suitable for small-scale studies because derivation of semivariograms for spatial dependence of soil properties is a complex process over large areas.

7 CONCLUSIONS

The acidification component developed for ARC/INFO has the potential to be used by land managers for studies of any scale, particularly if the component is improved into a formal computer program. This component would provide a valu-

able basis for future work in developing a more accurate, complete, and efficient program for acidification risk assessments.

A very important application of this acidification risk assessment technique is in assisting land managers to identify areas that are at high risk of soil acidification because soil acidity is largely an "invisible" problem until the situation is critical. It is anticipated that the methodology developed here may be applied to soils in agricultural regions throughout the world for improving the way in which acid soils are managed. Furthermore, the process has also been developed to create lime recommendation maps as well as maps showing the predicted pH at any given number of years from the present.

Suitable methodology for using geographic information systems to perform spatial analysis on a soil acidification data set is now available. The methodology used is an appropriate framework for soil acidification assessments. In particular, GIS is well suited to storing the case study data, performing spatial analyses, and presenting the output.

ACKNOWLEDGMENTS

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8

Micro- and Macroscale Heterogeneity of Soil Acidity

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1   INTRODUCTION

Soil properties vary on all scales of observation. Nevertheless, we think of soils predominantly in terms of homogeneous material. To think in this way might be justified for the agricultural soils that have been homogenized by plowing. Such simplifications are useful in developing concepts and models. However, only minimum tillage or no tillage is applied to a large portion of agricultural land, and for most forest ecosystems, homogenization by plowing has never been done. Moreover, in acidified soils burrowing and homogenizing animals, such as earthworms, diminish. It is therefore worthwhile to study the heterogeneity of soils.

Soil acidity limits plant growth. The release of Al into the soil solution as a result of proton buffering is suggested to have effects on root growth and nutrient uptake [1,2]. In water culture experiments, the ratios Ca/Al and Mg/Al, rather than the Al concentration itself, is an indicator of the root damage [2–5]. The significance of these ratios for root activity under field conditions, especially for mature trees, however, is still under discussion [6]. Nevertheless, the Ca/Al and Mg/Al ratios are often used to estimate the detrimental effects of soil acidification on trees and for the calculation of critical loads for acid deposition [6–8].

Aluminum inhibits Ca uptake by blocking Ca^{2+} channels in the plasma membrane [9] and Mg uptake by blocking the binding sites of transport proteins [10]. A high concentration of Mn^{2+} also inhibits Ca and particularly Mg uptake. On the other hand, the K uptake is not affected by Al or Mn [11,12].

The soil acidification of forest ecosystems has been dominated by anthropogenic atmospheric deposition in past decades, especially in the northern hemisphere [13,14]. However, in the last 15 years, the emission of SO_2 and subsequently the deposition of H^+ and SO_4^{2-} in forest ecosystems in Europe and Northern America have decreased substantially, but N deposition remains high [15–17].

Temporal and spatial variation in deposition as well as different filter properties of trees cause a heterogeneous pattern in soil input [18]. Connected with spatially different buffering and exchange capabilities, the spatial and temporal heterogeneity in soil properties emerges, leading to acidic "hot spots" as well as short-time bursts in H^+ activity.

Two aspects of heterogeneity are focused on in this chapter: (1) the consequences of soil heterogeneity for representative sample collection and data interpretation and (2) the effects of soil heterogeneity and the acidic pattern on root and plant growth and calculation of critical loads.

2   CASE STUDIES

Some investigations have been done on spatial and temporal heterogeneity of soil solution chemistry in forest ecosystems [19–27]. However, the numbers of samples in these investigations were low or the investigations were carried out for only a short time.

For a long-term investigation of soil heterogeneity at different spatial scales, a catchment in southeast Germany was fitted out with the measurement equipment for deposition, soil solution, and runoff monitoring [18,28,29]. Results from these investigations and from a state soil investigation in Germany [30] are presented here as case studies.

2.1   Sites and Measurements

The Lehstenbach catchment covers 420 ha and is located in the Fichtelgebirge, a mountain range in northeast Bavaria (Germany). This area is characterized by yearly average temperatures of 6.0°C (1987 to 2000, minimum 4.1°C, maximum 7.2°C) and annual precipitation rates from 623 to 1270 mm (average 929 mm). The annual throughfall is 573 to 952 mm (average 727 mm) and the seepage 256 to 684 mm (average 489 mm). The altitude ranges from 700 to 877 m above sea level. Close to 90% of the catchment is covered by Norway spruce [*Picea abies* (L.) Karst.] with an average age of 50 years [31].

At the Lehstenbach catchment, the granite bedrock is deeply weathered and strongly heterogeneous down to 30 to 40 m in depth. Among the soils, dystric cambisols predominate. Peaty soils and bogs cover one third of the catchment. The catchment is drained by a dense and irregular network of brooks and ditches. The altitude of the catchment is 690 to 877 m above sea level. Mean annual precipitation is up to 1100 mm. Annual average temperature at the mountain top (1992 to 2000) is 5.7°C (minimum 4.0°C, maximum 6.7°C). Approximately 90% of the catchment is covered with a spruce forest.

For *microscale* investigations 60 microsuction cups and 45 microtensiometers, each 1 mm in diameter and 5 mm in length, were installed in one wall of a small soil pit on a systematic grid (2 cm $\times$ 2 cm) at the Coulissenhieb site. The installation covered a soil depth to about 20 cm and an area of 180 cm^2 in total, ranging from the upper A to the B$_v$ horizon. Further details are given in Ref. 32.

Typical sampling volumes from the microsuction cups ranged from 0.05 to 1.5 mL of soil solution, with an average of 0.58 mL. Soil suction data were collected at a sampling rate of one per minute and condensed to a 10-minute average. The 48 soil matrix samples were taken in two areas of 8.5 cm^2. The horizontal and vertical spacing of the sampling was 15 mm. For the sampling, a stainless steel tube (sample volume about 2 cm^3) was used.

At the Coulissenhieb, a part of the Lehstenbach catchment, *mesoscale* investigations were performed. The investigation site was 2.7 ha. Underneath a 140-year-old Norway spruce stand, understory vegetation was rather sparse, comprising *Deschampsia flexuosa, Vaccinium myrtillus,* and *Calamagrostis villosa.* Twenty throughfall samplers, five suction cups, and tensiometers at 20, 35, and 90 cm depth, respectively, were installed with 2 m distance along four lines. Throughfall samplers and suction cups were sampled twice weekly. The temporal resolution of tensiometers was 1 hour.

At the *macroscale,* water and element fluxes (bulk precipitation, throughfall, transpiration, evaporation, seepage, and catchment runoff) have been measured continuously at up to 10 plots in the catchment. Soil matrix potentials and soil water contents have been measured hourly. Soil solution, groundwater, springs, and brooks have been sampled fortnightly. Soil matrix has been studied intensively at six main study sites as well as at the catchment scale. For the determination of sorbed SO$_4^{2-}$, soil samples were taken within the catchment on a systematic grid with a mesh distance of 300 m and with four replicates at each mesh intersection [33,34].

For the *regional scale,* data from the soil state survey (BZE [35]) from the German states Lower Saxony and Saxony were compiled.

Because timber increment data were not available for the Lehstenbach catchment, a comparison between the soil chemical data and the increment from the Solling site was performed. This site has similar stocking and a similar soil state. The Solling area is located in the southern part of Lower Saxony in north-

west Germany (51°45′ N, 9°34′ E). Mean temperature is 6.5°C and annual precipitation is 1088 mm year^{-1}. The plot is located about 500 m above sea level and vegetated by a 117-year-old Norway spruce plantation. A detailed description of the plot has been given in Ref. 36.

The volumetric timber increment was determined by measuring the diameter and height of all trees at the site yearly from 1967 until 1972 and then in 1977, 1980, 1981, 1985, 1990, 1996, and 2000.

2.2 Analytical Methods

Chemical analysis of soil solutions collected by the microsuction cups (Cl^-, SO_4^{2-}, NO_3^-) was done by capillary electrophoresis [37] and ion-sensitive field effect transistor (ISFET) pH measurements. The soil solution collected from the normal-sized suction cups as well as water samples were analyzed by ion chromatography (Cl^-, NO_3^-, SO_4^{2-}). The pH was measured with a glass electrode.

Chemical analyses of soil samples were carried out sequentially on initially 1-g samples. Soil suspensions were diluted to 10 cm^3, shaken for 1 hour, and centrifuged. In the supernatant, SO_4^{2-} was measured by ion chromatography.

Desorbed SO_4^{2-} was determined at all scales by percolating field-moist samples with H_2O. The data were fitted nonlinearly to a modified Langmuir isotherm. Further details are given in Refs. 34 and 38.

2.3 Mathematical Methods and Modeling

Water fluxes in soil were calculated for each point by a numerical simulation model. The ion fluxes at each lysimeter were established by multiplying the simulated water fluxes by the ion concentrations on a fortnightly basis [18].

The model MAGIC (Model of Acidification of Groundwater in Catchments [39]) was employed to evaluate the effect of spatially different sorption/desorption isotherm parameters on long-term SO_4^{2-} dynamics prediction. The model describes cation exchange as an equilibrium reaction between the base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and Al. For details see Refs. 33 and 34.

The number of samples required to match the population average can be calculated if the desired statistical precision is fixed. The computations followed the equation [40]

$$n_{\bar{x}} = \frac{z_\alpha}{\bar{x} - \mu} \sigma^2$$

where $n_{\bar{x}}$ is the minimal number of samples, z_α the z value (1.96 for $\alpha = 0.05$ was used here), $\bar{x} - \mu$ the demanded precision, and σ the standard deviation of the population. In this case σ had to be estimated conservatively with $\sigma = s$, where s

was the standard deviation of the sample. The precision $\bar{x} - \mu$ was fixed to $\pm 10\%$ of the corresponding fortnightly average, which can be seen as a moderate requirement. The computation required a normal distribution of the underlying data. This was tested by the *W*-statistic test [41,42] for each ion, each compartment, and each sampling date. The zero hypothesis, that the values are normally distributed, could not be rejected at the 99% significance level.

2.4 Results

2.4.1 Input, Soil, and Runoff Heterogeneity of Matter Fluxes

For the assessment of the soil heterogeneity, it is important to compare it with input and runoff heterogeneity. A considerable part of heterogeneity emerges from the trees as structural elements while combing out reactive gaseous constituents from the atmosphere (e.g., SO_2 and NO_x). These constituents are dissolved in the water film at the leaf surface, and subsequently the reactants are released (SO_4^{2-}, NO_3^-) accompanied by base cations to the throughfall water. The throughfall water is distributed in specific patterns by the leaves as well as by the stem and crown structure. This leaching from canopy can change element fluxes with throughfall considerably, especially nitrogen and proton fluxes [43,44]. In particular, stem flow can evoke acidic hot spots in the soil around the trees [25].

Another source of heterogeneity is the soil structure with different reaction compartments. In fast-draining pores, water can pass through the soil without major chemical reactions with the soil surface. In contrast, in slow-draining pores the water can equilibrate with the soil surface and the pore water. Thus, the chemical composition of the draining water will change in accordance with a decreasing pore diameter. The travel time of the water depends on the rainfall intensity, soil water status (wet, dry), hydraulic gradient, and local soil structure (relative proportions of coarse and fine pores). The extent of element loading from the soil into the passing water depends on the actual exchange capacity of the local soil surface, chemical reactions (such as mineralization), a lack or surplus of the transported water, and root uptake.

Figure 1 shows the coefficients of variance for pH, SO_4^{2-}, and NO_3^- for four compartments: precipitation, throughfall, mineral soil, and runoff. The variance in precipitation is lowest of all compartments. A great increase in heterogeneity for all elements except Cl^- can be observed in throughfall when the water has passed the crown compartment. The maximum heterogeneity is reached in soil solution at 20-cm depth. With increasing soil depth, this influence diminishes. In runoff, heterogeneity reaches the level of variance in the precipitation.

For Cl^- the findings are different. This is because Cl^- is a more or less inert element with respect to the soil. Therefore, the heterogeneity does not increase in soil solution. Nevertheless, the heterogeneity increases drastically in runoff as an effect of thawing salt infiltrating from a nearby country road.
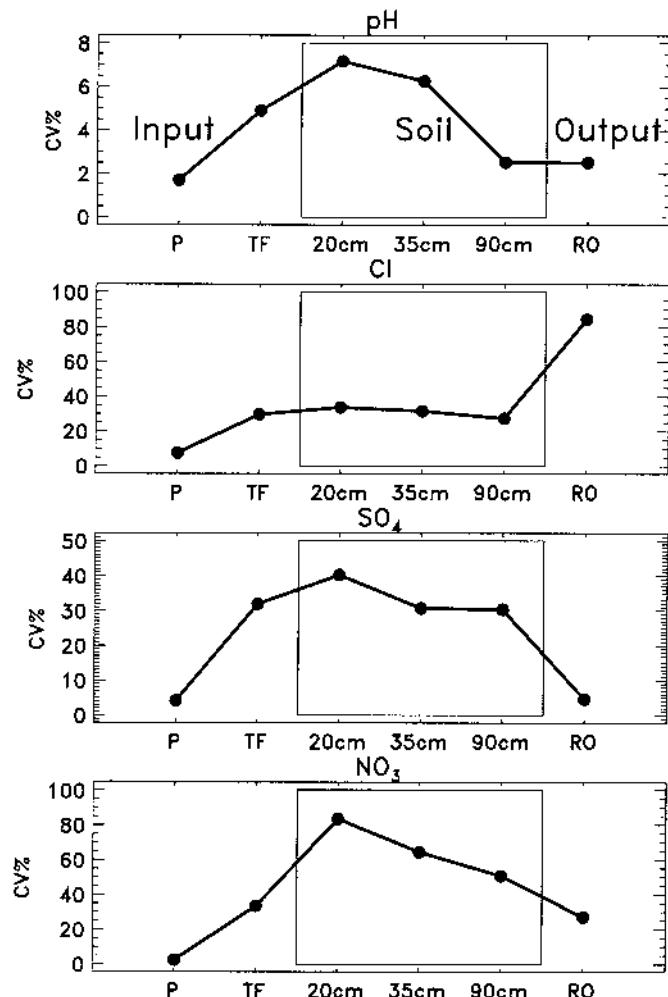
FIGURE 1 Coefficient of variation (CV%) in precipitation (P), throughfall (TF), soil solution at different depths (20, 35, and 90 cm), and runoff (RO) for pH, Cl^-, SO_4^{2-} and NO_3^-. The coefficient of variation has been calculated separately for the various sampling dates; only averages of these values are given. The data correspond to samples obtained from 1993 to 1999.

Therefore, to minimize sampling efforts for the investigation of mass balance, it would be best to investigate the fluxes in precipitation and runoff. However, with precipitation, only wet deposition is recorded. Other methods for recording dry deposition, such as surrogate surfaces or concentration gradient methods (eddy correlation), are representative only for larger scales in space and time or require uniform vegetation and adequate fetch [45]. However, for all methods it is true that the determination of total deposition from throughfall yields an underestimate of the actual deposition because the intake at the crown by needles and leaves is neglected [46].

At the runoff of a whole catchment, the heterogeneity will decrease with an increase in the portion of deep seepage water compared with the surface water (Fig. 2). On the other hand, runoff is often an unreliable estimate of the output flux with respect to unknown sinks or sources of water in the catchment (e.g., seepage in catchments that are not leakproof) and elements (e.g., fens). In addition, statements are possible only for the entire catchment, not for individual stands. Therefore, the only way to obtain representative results in such heterogeneous systems is to work with appropriate sampling sizes.

Ågren and Bosatta [47] suggested evaluating nitrogen saturation of terrestrial ecosystems for mass balances. In Fig. 3 the input–output mass balances for
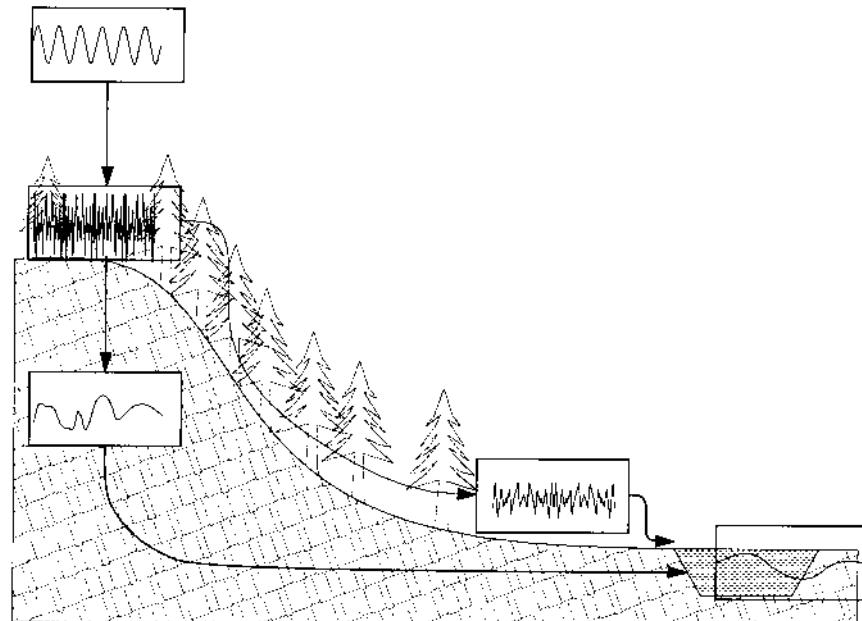
FIGURE 2 Heterogeneity of input and output fluxes in the catchment.
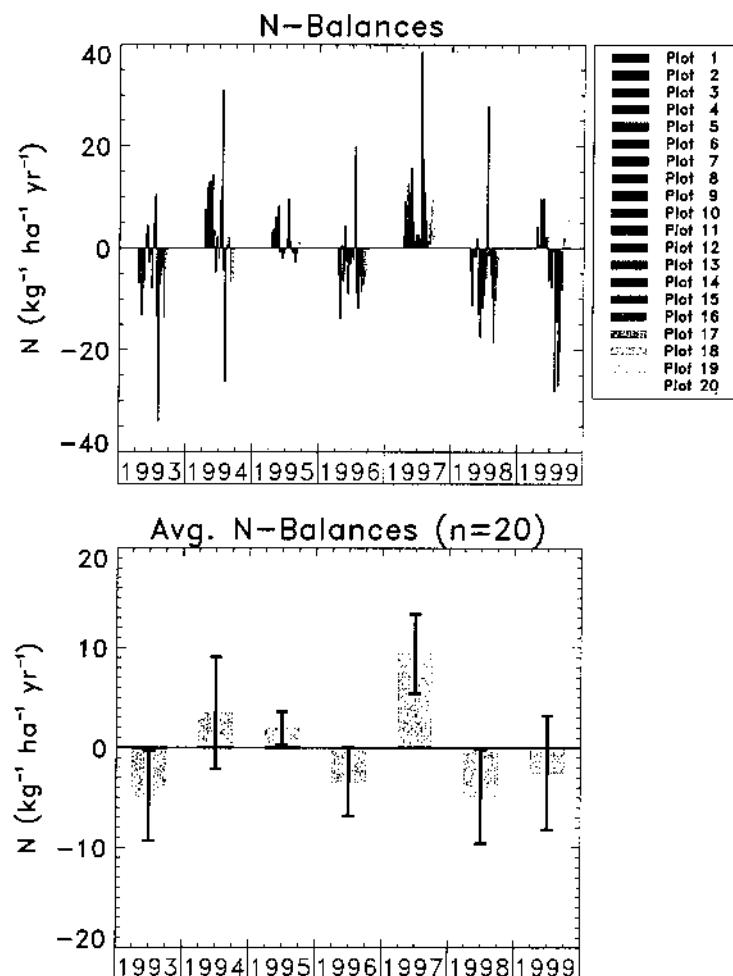
FIGURE 3 Annual input–output balances (throughfall-seepage at 90 cm depth) of nitrogen (NO_3-N $+NH_4$-N) for the Coulissenhieb site, 1993–1999. (Top) Annual balances for 20 plots at the site; (bottom) average and 95% confidence interval for the 20 plots.

nitrogen are presented. Spatial heterogeneity of the 20 plots and temporal heterogeneity over the 7 years are obvious (Fig. 3, top). The balances are positive or negative over the years. It is obvious that results that consider only one or a few plots, e.g., when a restricted sampling size is taken into account, could be misleading.

The 95% confidence intervals (Fig. 3, bottom) often include zero. For this reason, evaluation of 20 plots did not provide grounds for a decision on whether those balances are positive, negative, or zero.

In general, to assess the ecosystem state by using nitrogen balances is very expensive (huge sampling effort) or very unreliable because of the limited sampling size. Because of these methological deficiencies, logging all relevant nitrogen fluxes is an obvious choice.

2.4.2   Spatial Heterogeneity and Scale Dependences

A way to minimize sampling size is to detect spatial dependences and to develop a stratified sampling design based on these dependences. Figures 4 and 5 show the heterogeneity in pH, NO_3^-, and SO_4^{2-} on the microscale (centimeters) and mesoscale (plots). No spatial correlation was found for pH with SO_4^{2-} or NO_3^-.
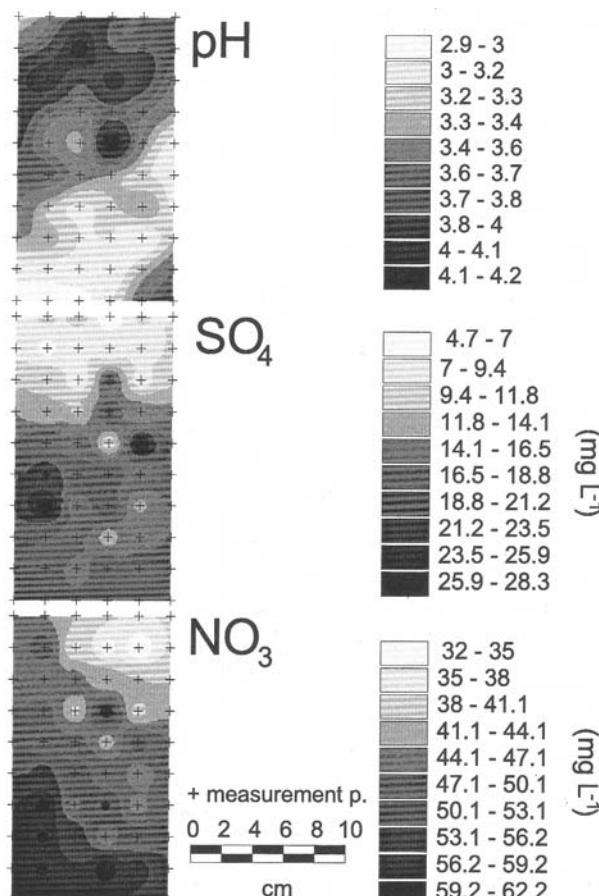
FIGURE 4   Spatial distribution of the pH, SO_4^{2-} and NO_3^- values as measured by microlysimeters on the microscale. Interpolation was done by inverse distance weighing.
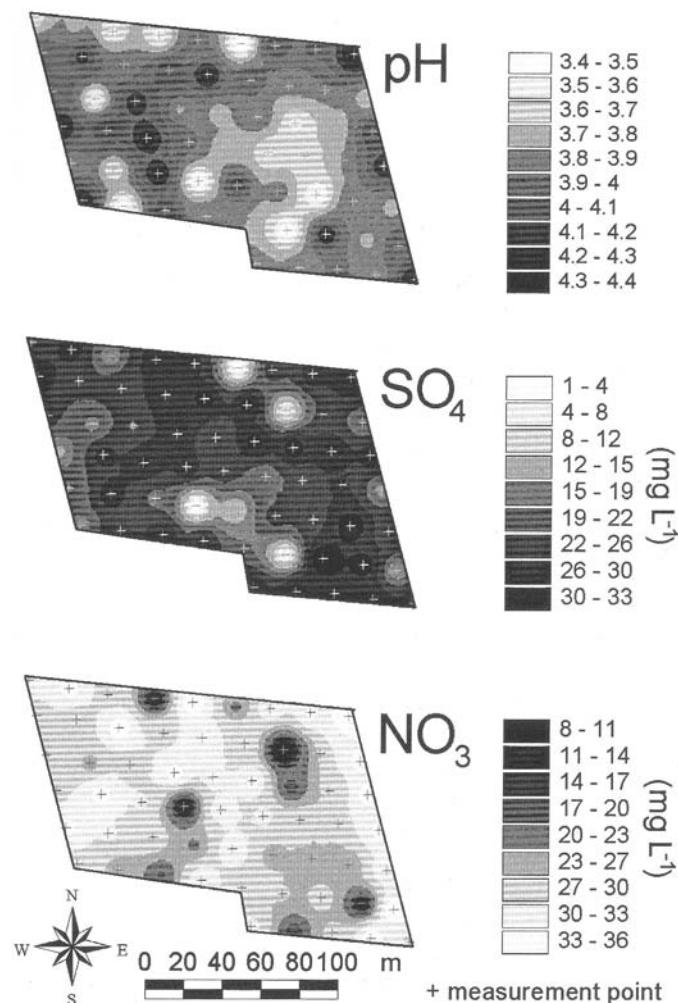
FIGURE 5 Spatial distribution of the pH, SO_4^{2-}, and NO_3^- values as measured by standard lysimeters on the macroscale. Interpolation was done by inverse distance weighing.

Scale-dependent variance of soil solution data is given in Table 1. Because spatial variability tends to decrease with depth [38], the intention was to obtain comparable depths. Mean values of the anion concentration at different scales differ by a factor of 2 to 3. Spatial heterogeneity of the ion concentration seems to be ion and scale specific. The coefficient of variance of NO_3^- is largest in the micro

to macro range. The number of required samples in Table 1 indicates that for NO_3^- up to 256 samples are required to determine the concentration with an accuracy of $\pm 10\%$. The coefficient of variation (CV) of pH has a maximum at the microscale, and the CV of Cl^- has a minimum at the macroscale. For SO_4^{2-}, there is a clear trend from maximum at the microscale to minimum at the macroscale.

TABLE 1 Characteristics of Soil Solution Sampled at Different Scales[a]

Scale and characteristics	Minimum	Maximum	Mean	CV (%)	N
Microscale (microcups), $n = 55$					
pH	3.3	5.0	4.0	8.0	1
SO_4	4.9	41.2	24.0	19.0	17
Cl	2.9	17.6	5.8	51.0	30
NO_3	0.0	20.4	3.3	129.0	108
Mesoscale (four subsites), $n = 20$					
pH	3.3	4.2	3.7	7.0	1
SO_4	3.8	33.8	16.4	33.0	36
Cl	0.9	8.6	2.3	40.0	8
NO_3	1.5	51.3	18.9	83.0	256
Mesoscale (25 m × 25 m grid), $n = 59$					
pH	3.4	4.4	3.8	7.0	1
SO_4	7.4	36.0	15.5	36.0	40
Cl	1.6	16.1	5.3	50.0	26
NO_3	0.0	40.1	10.5	77.0	123
Macroscale (different stands), $n = 6$					
pH	3.3	5.1	4.3	5.0	1
SO_4	2.1	72.0	30.9	56.0	190
Cl	0.9	8.6	2.6	26.0	4
NO_3	0.0	51.3	4.5	100.0	89

[a] Micro suction cups were positioned 12 to 28 cm deep, standard suction cups 20 cm deep (4 × 5 suction cups), 35 cm (25 m × 25 m grid) and 50 cm deep at the watershed scale. n = number of samples per date, N = required sampling size. Mean and coefficient of variance have been calculated for various sampling dates separately, and median values were presented.

Analysis of correlation length was performed for soil solution samples by semivariograms. For microsuction cups, which covered a field of 8.14 cm^2, the correlation length is beyond the scale of the measurements. For the 25 m $\times$ 25 m grid, the correlation length is apparently less than the minimum sampling distance for all ions under study.

At the spatial scale for a whole state (Lower Saxony, Fig. 6), the heterogeneity of pH follows spacious geological formations: the Pleistocene sands in the north are associated with low pH, whereas in the south in the Lower Saxony mountainous region more base-rich rock formations, partially with lime, are associated with higher pH.

2.4.3   Temporal Heterogeneity of Soil Solution

From Fig. 7 (left side), the large temporal heterogeneity of SO_4^{2-} concentrations in soil solution is obvious, especially in throughfall during the winter months due to the combustion of heating oil. This dynamics can also be seen in runoff but not in soil solution.

In general, a trend of diminishing SO_4^{2-} concentrations in throughfall is clear. The concentrations in discharge and runoff follow the input trend. With the concentration decrease, the standard deviation decreases (Fig. 7, right side); i.e., the absolute variability decreases with decreasing concentrations. On the other
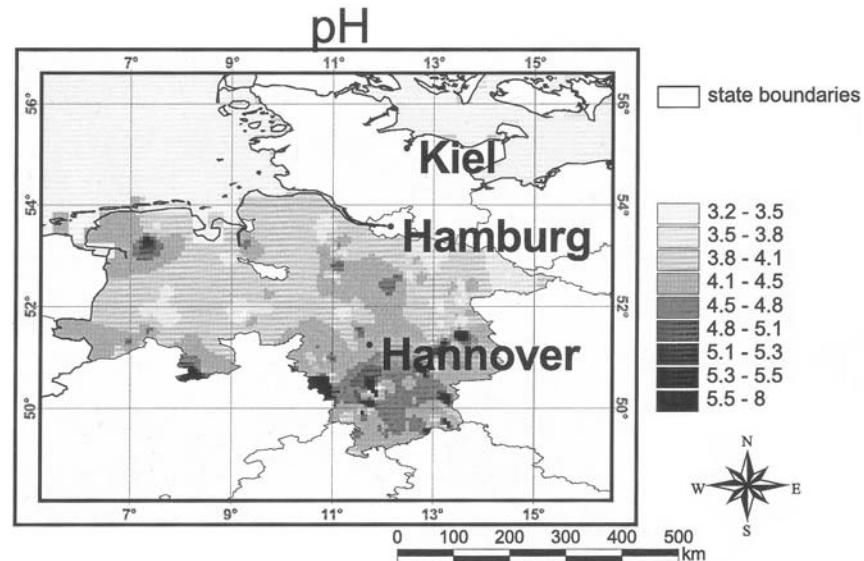
FIGURE 6   Distribution of the pH values on the metascale as measured by BZE. Interpolation was done by inverse distance weighing.
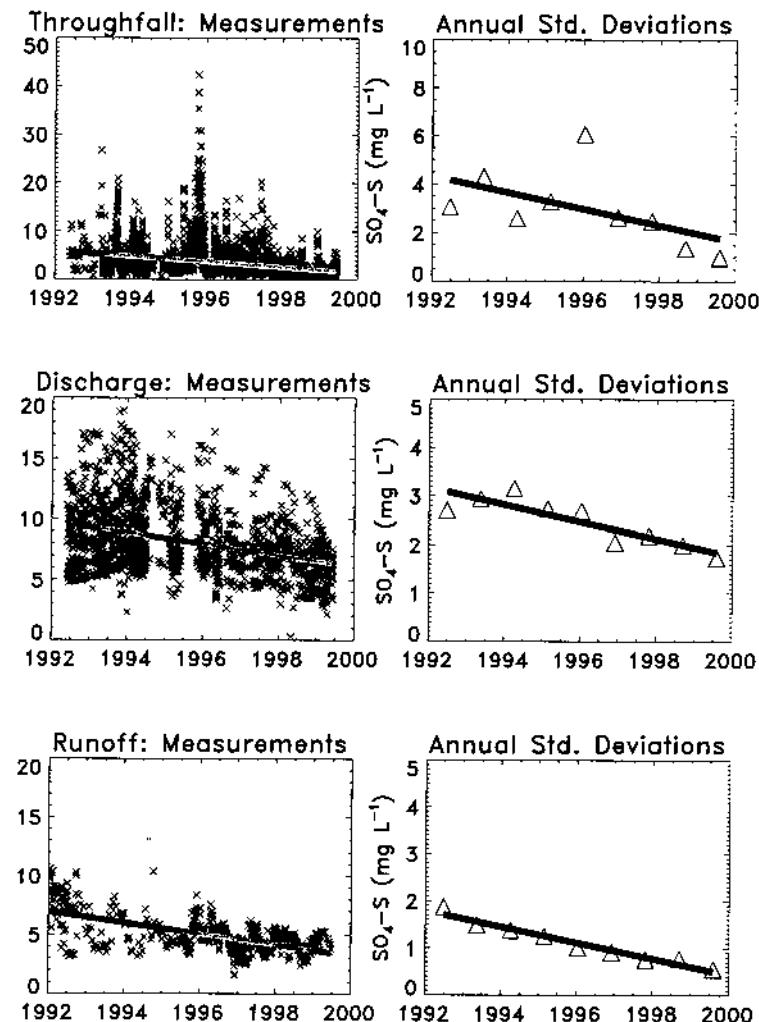
FIGURE 7 Temporal heterogeneity of SO_4^{2-} concentration in throughfall, soil solution, and runoff. (Left) Single values and trend lines of the biweekly concentration measurements; (right) annual standard deviations and trend lines.

hand, the variation coefficient (i.e., the relative variability related to the average concentrations) remains unchanged (not shown).

2.4.4 Heterogeneity and Model Application

Results for SO_4^{2-} extracted from soil samples are listed in Table 2. The mean values decrease with scale by a factor of 3.5, whereas standard deviation increases by

TABLE 2 H$_2$O-Extractale SO$_4^{2-}$ (μmol g^{-1}) in B Horizons at Different Scales

Scale and horizon[a]	Minimum	Maximum	Mean	CV (%)[b]
Microscale				
B$_{hs}$	3.31	5.07	3.94	12.1
B$_s$	3.34	5.14	4.13	12.8
B$_v$	3.75	4.93	4.16	8.9
Total	3.31	5.14	4.09	11.2
Mesoscale				
B$_{sh}$	0.48	2.98	1.49	56.4
B$_s$	1.07	2.86	1.84	30.4
B$_v$	0.68	3.93	1.72	48.3
Total	0.48	3.93	1.63	49.7
Macroscale				
B$_{sh}$	0.14	0.78	0.47	48.9
B$_s$	0.20	2.98	1.42	60.6
B$_v$	0.13	2.75	1.22	74.6
Total	0.13	4.61	1.19	78.2

[a] B$_{hs}$ and B$_{sh}$ are B horizons influenced by sesquioxides and humic substances, B$_s$ is a B horizon influenced only by sesquioxides, and B$_v$ is a weathered B horizon.
[b] CV, coefficient of variation.

a factor of 2, resulting in an increase in the coefficient of variation by approximately seven-fold.

In Table 3, model results are given for the range of measured isotherm parameters. Variation of isotherm parameters does not increase substantially with scale. As the SO$_4^{2-}$ concentration in the soil solution is near the maximum adsorption capacity of the soils, the effect of different isotherm parameters increases with decreasing SO$_4^{2-}$ deposition. Thus, differences in predicted SO$_4^{2-}$ concentration in the soil solution are most pronounced at approximately the year 2005. Fur-

TABLE 3 Simulation of the Sulfate Concentration with the MAGIC Model[a]

	b (mmol$_c$ kg)$^{-1}$	$C_{b/2}$ (mmol$_c$ m^{-1})	SO$_4$ 1992 (mmol$_c$ m^{-1})	SO$_4$ 2005 (mmol$_c$ m^{-1})	SO$_4$ 2044 (mmol$_c$ m^{-1})
Maximum	12.6	738.8	624.3	368.1	175.4
Upper	8.2	122.1	567.3	303.7	169.8
Mean	*4.6*	*149.3*	*552.5*	*273.1*	*161.9*
Lower	2.8	1796.0	544.7	227.5	159.1
Minimum	0.6	54.2	533.1	211.5	159.4

[a] b = sorption maximum (μmol g^{-1}), $1/k$ = half-maximum saturation point (mmol L^{-1}), which is equal to the SO$_4^{2-}$ concentration at $\frac{1}{2}$ b. SO$_4$ 1992, SO$_4$ 2005, and SO$_4$ 2044 are the simulated SO$_4^{2-}$ amounts per meter of soil for the years 1992, 2005, and 2044, respectively.

ther decreasing SO_4^{2-} deposition decreases the influence of the shape of the isotherm curves, thus reducing spatial variation again.

2.4.5 Soil Chemistry and Timber Increment

The yield tables from Schober [48] allow comparison of the measured tree growth with a reference curve derived from long-term observations. In Fig. 8 the increment of the Solling site is compared with the yield table values. The increment developed from yield class III in 1965 to yield class I in 2000 (Fig. 8, bottom) in spite of the decreasing Ca/Al and Mg/Al ratios (Fig. 8, top).
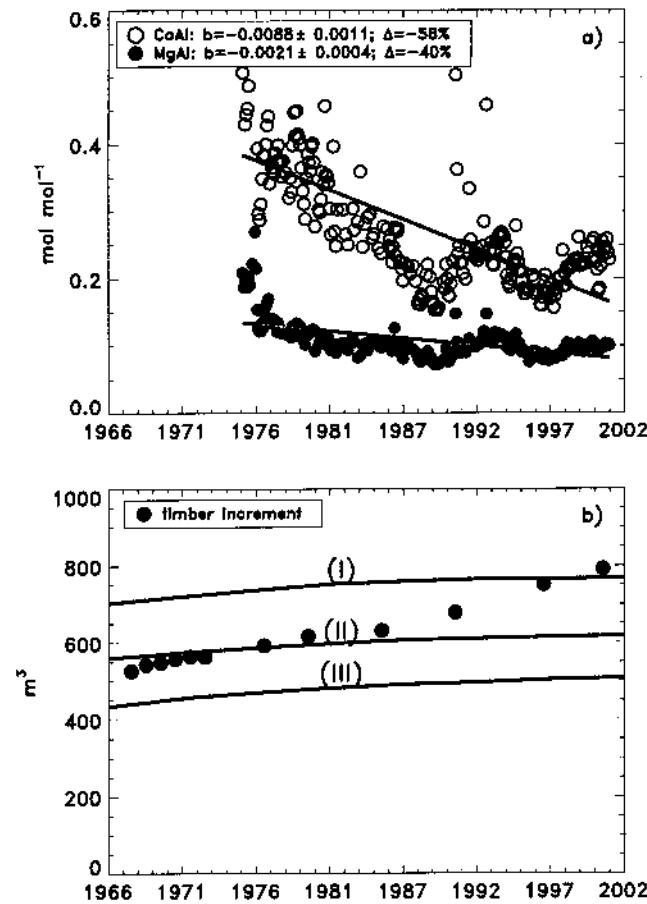
FIGURE 8   (Top) Time course of Ca/Al and Mg/Al ratios, with trend lines. (Bottom) Development of timber increment at the Solling site (·). For comparison, the yield table values for the site class I from yield table (upper line), site class II (middle line), and site class III are presented.

3 IMPLICATIONS

Two main aspects should be considered when investigating soil acidity. First is the soil–plant interaction aspect. Because of nutrient depletion and release of substances that are toxic to roots, a yield decrease is expected. On the other hand, an environmental aspect is the concern about the impairment of the sustainable yield potential of the soils and the release of detrimental substances from the soil to the environment.

Heterogeneity in soil solution for most elements is much higher than in throughfall or runoff. This has implications for *soil–plant interactions.* As in Figs. 5 and 6, the spatial pattern of soil fertility can be assumed for all soils. Dealing with this is different for different land uses. When growing an arable crop, the actual soil state can be deduced from the yield after harvesting. Deteriorated soil conditions will be indicated by a lower yield or changes in the plant content of various substances. Lowering yield can be alleviated by fertilizing and liming according to the yield pattern. The heterogeneity of the soil conditions and the different fertilizer demand can be manipulated through precision farming.

In forestry, the situation is more difficult. Fertilizer is hardly applied to forest soils for economic reasons. Because of the long-term harvesting periods in forestry, it is impossible to infer the actual soil state from the harvest. However, permanent increment measurements can fill the gap but are expensive and practicable only for a few trees.

As shown in Fig. 8, the spruce increment does not seem to reflect the deteriorated soil state as indicated by the Ca/Al or Mg/Al indicators. On the contrary, the spruce goes above the increment as defined by the conventional yield tables. Also, the element contents in the needles do not reflect the actual soil state [49].

One hypothetical explanation for this phenomenon is that high nitrogen inputs are responsible for the unexpected increment of the last decades. This was unexpected because the soil state indicated that sufficient nutrients, especially Mg could not be taken up by the roots. A suggestion was offered that Mg and other nutrients can be translocated from older needles into growing tips [50,51]. However, on a long-term basis this would lead to a shortage of Mg and other nutrients because of losses. Therefore, the long-lasting increment can be explained only partly by this hypothesis.

Part of this phenomenon can be explained by soil heterogeneity. The Ca/Al and Mg/Al indicator has been deduced from hydroponics experiments, i.e., an absolute homogeneous environment for the root. Under field conditions, the Ca/Al values measured in lysimeters may not reflect the actual soil state as seen by the tree roots. First, it does not reflect the fact that roots can grow to the soil organic horizon to explore the nutrients from the yield.

The soil water from fast-draining pores is overrepresented in the collected lysimeter water. Lysimeters collect relatively more water from the fast-draining

pores because of the limited suction (200–300 mbar) at which the lysimeters were maintained. Further, they collect unspecific water, but not in the microcompartments from which the roots take up water and nutrients. The fast-draining pores seem to be hardly used by the tree roots because the pores are quickly filled with the infiltrating water but also as quickly emptied because the water is not retained against gravity. Therefore, this pore class is less suitable for sustainable water supply for roots. Tree roots have sufficient dynamics to avoid such detrimental zones and to search actively for more suitable microcompartments. Nutrient- and base-rich water is more likely to be found in smaller pores because the time the water can come in equilibrium with the cations from the mineral surface is longer.

Thus, the soil situation might look worse when analyzing the lysimeter water compared with the actual situation experienced by the roots. In this sense, soil heterogeneity can contribute to the survival of trees in otherwise unfavorable environmental conditions. Therefore, indicators such as Ca/Al should not be directly transferred from hydroponics experiments. To characterize the effective soil state under field conditions, spatial and temporal distributions seem to be more suitable.

Maps of the spatial distribution of the element concentrations, especially those measured in microlysimeters, might yield further insights into whether the soil has enough microcompartments with suitable living conditions for roots. Micro scale heterogeneity of soil solution should especially be considered when investigating root uptake because roots are very dynamic in avoiding detrimental soil zones and finding nutrients. An acidification indicator averaging different soil horizons could be misleading. This is confirmed by studies showing that soil acidification will decrease the fine root mass of trees and shift the rooting zone to upper, more nutrient-rich soil layers [52,53].

The reaction of the trees to increasing soil acidity cannot be understood without analyzing the temporal and spatial variability of acid stress [54]. Studies of resource distribution in forested ecosystems need to consider not only the average levels but also the variance, frequency, and spatial distributions of these resources [55]. In middle Europe, the concentrations of SO_4^{2-} in precipitation and throughfall are decreasing. In parallel, the variability is decreasing, as can be seen from Fig. 7, with the consequence that acid stress by sulfate peaks is reduced.

The time dependence of spatial variability is also illustrated by the application of the MAGIC model. The variation of isotherm parameters influences the variability of the computed SO_4^{2-} concentration in soil solution. Without knowledge and use of isotherm variability, no statements about modeling insecurities are possible. Model results without an estimate of the error range of the results provide limited evidence.

The correctness of the critical loads approach for acidic deposition into forest soils is questionable [6]. The problem demands a more dynamic approach that takes into account the temporal and spatial variability of terrestrial ecosystems. According to Ulrich and Summer [56], under high acid deposition and on less

buffered soils, short-term strain (temporal heterogeneity) will occur more often and so destabilize the ecosystem.

Due to the long-distance transports of the gaseous components, critical loads are spatially applicable only. One should commit critical levels means to consider the weakest link. However, at the site of the strong heterogeneity, one is not likely to find any region that will not have at least a few very sensitive spots. As a consequence, the acidic emissions have to be further reduced to accommodate the sensitive spots.

Important for *environmental aspects* are balances and fluxes of the matter in ecosystems because they indicate nutrient losses for the system or the release of detrimental substances to adjacent ecosystems.

It has been demonstrated that the degree of heterogeneity at a given observational scale is strongly dependent on the chemical species considered; e.g., NO_3^- in soil solution seems to be especially costly to measure adequately with a prescribed accuracy. Because of the heterogeneity, a large number of replications are necessary [18]. The fluxes of matter can, with reasonable efforts, be calculated only with limited precision. Spatial heterogeneity at all scales has to be taken into account. To determine the average with an appropriate accuracy sampling, up to 256 replicates are necessary for soil water, as found in this study. Conclusions from investigation of the matter flux have to consider the error ranges. However, due to errors, the sharpness of the statements decreases and recommendations, e.g., on fertilizing, become imprecise. The utilization of input–output balances to characterize ecosystem states of N saturation is especially unreliable and limits practical importance. Small-scale spatial and temporal variation occurs. The state of N saturation can vary spatially at small scales, as shown in Fig. 3. These dynamics in soil have been investigated as fingering [57]. The temporal dynamics of the state of N saturation have the consequence that balances at one plot differ from year to year, which makes statements on N saturation unreliable. This complicates concrete measures (opening up, tillage) to manipulate the N pool in the ecosystem.

Variogram analysis gave evidence that correlation length is between the resolution of the micro- and the normal-sized soil suction cups (2 cm and 2 m, respectively). This is in accordance with, e.g., Simmonds and Northcliff [58], who determined a correlation length of Br^- and Cl^- transport in a sandy loam of approximately 35 cm. The dependence of NO_3^- concentration in soil solution and catchment runoff on a variety of different parameters (Table 2) indicates that different deterministic length scales overlap. For the investigated sites this would indicate that no additional heterogeneity can be found on the macroscale.

4   CONCLUSIONS

Measurement concepts should consider intensive spatial and temporal investigations of relatively small plots. They will be representative of the surroundings. In-

tensive measurement plots seem more appropriate for further understanding of soil reactions and the integration of heterogeneity in the evaluation. Spacious assessment based on the almost uncertain estimation of local soil properties by means of geographic information systems is inadequate because the validity and implications for the ecosystem of such results cannot be estimated at present.

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9

Measurements of H$^+$ Fluxes and Concentrations in the Rhizosphere

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1 INTRODUCTION

Soil pH is probably the most important chemical soil parameter [1]. It reflects the overall chemical status of the soil and influences a whole range of chemical and biological processes occurring in the soil. Because of its implications in most chemical reactions in the soil, knowing the actual value of soil pH and monitoring its changes is critical for understanding the physicochemical functioning of the soil.

During plant growth, roots exchange a number of substances with their environment, thus ultimately modifying the physicochemical conditions of the soil solution, its pH in particular [2,3]. These pH changes result mainly from two processes. First, roots and rhizosphere microorganisms rely on root exudates to produce CO_2 through respiration. The buildup of CO_2 partial pressure thereby occurring in the rhizosphere can contribute to some acidification [4]. In acid soils this is of restricted significance, as at low pH carbonic acid remains mostly undissociated in the soil solution, its first pK being 6.36 [5]. The second and major origin of pH changes in the rhizosphere is related to the release of H$^+$ or OH$^-$ to counterbalance a net excess of cations or anions, respectively, entering the roots [6,7].

For further details on this cation–anion balance, the readers are referred to Chapter 3 in this book. These processes can be affected by environmental stresses; Fe deficiency [8] and P deficiency, the latter being more relevant for acid soil conditions, can both enhance H^+ release by plant roots [9,10]. Aluminum toxicity is another common stress that plants can experience in acid soils and which can influence these processes. Indeed, as reported for corn, for instance, Al toxicity results in enhanced H^+ release via a reduction of nitrate uptake and little concomitant effect on cation uptake, especially so in Al-sensitive genotypes [11–13]. For an extensive review of the diverse origins of root-induced pH changes that can occur in the rhizosphere, see Nye [6,14], Haynes [7], Marschner [2], or Hinsinger [3].

The actions exerted by roots are localized and confined to the rhizosphere, i.e., the volume of soil that is directly influenced by plant roots [15]. The resulting changes in pH can be considerable, reaching one to two pH units [2,3,16]. Such changes are of major ecological significance because of their possible effects on the physiological activity of the roots and rhizosphere microorganisms and because of their influence on the bioavailability of mineral nutrients and potentially toxic substances in soil. It is therefore of prime importance to take account of H^+ fluxes occurring in the rhizosphere and to have access to the actual values of pH that plant roots can experience. The aim of this chapter is to review the techniques developed for this purpose. As the rhizosphere is a restricted volume of soil around roots that is rather difficult to access for in situ and to sample for ex situ measurements, a range of methods have been designed to overcome this major difficulty. The advantages and major limitations of each of these approaches will be discussed. The first part will focus on the methods used for measuring H^+ ions that are released or taken up by roots growing in solution culture, without any solid phase. The second part will review the methods used for measuring the induced pH changes in the rhizosphere of soil-grown plants. This chapter will show that, in spite of the considerable advances in the knowledge of the physiological functioning of roots in controlled, more or less artificial conditions, the various consequences in terms of pH changes in natural conditions, and more generally of physicochemical conditions in the rhizosphere, are still largely unknown. This is mainly due to the many methodological difficulties encountered in measuring soil parameters that are as crucial as pH at the scale relevant to the rhizosphere.

2 MEASUREMENTS OF FLUXES OF H^+ RELEASED BY ROOTS IN SOLUTION

2.1 Measurements by Titrimetry

When plants grow in solution, the net amounts of H^+ released by the whole root system can be measured by monitoring the changes in the solution pH as a function of incubation or culture duration. The given amount of H^+ ($\Delta[H^+]$) released

by roots is related to the pH change in the solution (ΔpH) according to the following relation:

$$\Delta[H^+] = -\beta\, \Delta pH \tag{1}$$

where β is the H^+ buffering capacity of the solution. Two methods are used: (1) the pH is not controlled during the period under study and samples of solutions are periodically back-titrated to the initial pH, making it possible to calculate the net H^+ fluxes corresponding to the variation of pH, or (2) the pH is maintained constant during the culture using a pH-stat device and the net H^+ fluxes are calculated from the amounts of base or acid added during the culture.

2.1.1 A Basic Method, the Back-Titration of Culture Solutions

The method of back-titration of solutions is simple to carry out and has therefore been used by many authors [17–21]. However, to get the actual fluxes of H^+ produced by root activity, the culture solution must have a constant and known, or very low and consequently negligible, buffering capacity. In the case of complete nutrient solutions, the buffering capacity results mainly from inorganic phosphate and carbonate. The concentration of carbonate in the bathing solution originates from respiration of roots or from the dissolution of gaseous CO_2 from the atmosphere. The main contribution of CO_2 to H^+ buffer capacity of the solution is due to the first dissociation of carbonic acid H_2CO_3 to H^+ and HCO_3^-; the pK of the reaction is 6.36 and the buffering capacity becomes important at pH greater than 6.0. Studies carried out on castor bean (*Ricinus communis* L.) plants grown at pH 6.5 with NO_3^- as the sole source of N demonstrated the importance of bicarbonate in the total amount of base (i.e., OH^- and HCO_3^-) excreted by the plants during the growth period [17]. Indeed, back-titration of the culture solution to the initial pH of 6.5 led to underestimation by 50% or more of the actual amount of base released by the plants. The total amount of base excreted could be calculated only from data obtained by titration to pH 4.5, when almost all HCO_3^- in the system was converted to H_2CO_3 and then evaporated to CO_2. Indeed, comparison of the HCO_3^- concentration in the culture medium after plant growth with the HCO_3^- concentration predicted from atmospheric CO_2 showed that aqueous H_3CO_3 was not in equilibrium with atmospheric CO_2; the solution was supersaturated to a considerable degree, suggesting a high concentration due to the respiratory activity of the roots together with a slow rate of evaporation of CO_2. On the contrary, with castor bean grown at pH 6.5 in NH_4^+-nutrient solution, the effects of phosphate uptake and ionic strength changes on base titrimetry of excreted H^+ were scarcely significant, with underestimation of H^+ release not greater than 3% [18]. In this case, NH_4^+ uptake resulted in an acidification of the solution to below pH 6.0. Under such conditions H_2CO_3 remained largely undissociated and hence root respiration did not contribute to acidification of the solution.

The reliability of the back-titration method strongly depends on the initial pH, the buffering capacity of the solution, and especially the concentration of bicarbonate, which may vary strongly during the measurement. In addition, the change in pH occurring during uptake or growth can modify the uptake rates of the ions under study. This problem was solved by using experimental devices that make it possible to automatically maintain the pH at its initial value, the so-called pH-stat devices.

2.1.2 The More Advanced pH-stat System

This method is based on continuous monitoring of the H^+ or ion under study with a pH electrode or an ion-specific electrode. The electrode is connected to dosing pumps that automatically deliver known volumes of solution when the actual H^+ or ion concentration deviates from its initial fixed value. In the case of H^+, such a system is called a pH-stat system and requires one or, if possible, two dosing pumps for adding acid or base to the culture solution according to the direction of pH change. The system can be computer controlled and maintain constant K^+ and NO_3^- [22], H^+ and NO_3^- [23], or only H^+ concentrations [24,25]. The net fluxes are then calculated from the successive additions of the solutions containing the ion considered. With this experimental system, it was confirmed that NO_3^- uptake by plant resulted in a net alkalinization of the solution [23,25], whereas NH_4^+ uptake resulted in a net acidification [25] (Fig. 1).

The main advantage of the pH-stat system is the possibility of monitoring over time the net fluxes of H^+ released by the whole root system and their kinetics as a function of any factor (such as the source of mineral N) without any significant changes in pH, which could in turn modify the uptake rate of other ions. However, the method does not make it possible to observe heterogeneities in root functioning. To address this question, it is necessary to use other local methods such as micropotentiometry.

2.2 Local Measurements by Micropotentiometry

2.2.1 Liquid Membrane Ion-Selective Microelectrode

Local net fluxes of H^+ can be determined with ion-selective microelectrodes. The main type of electrode used for ion flux measurements in solution is the liquid membrane microelectrode. Lucas and Kochian [26] initiated this technique to estimate the net flux of H^+ from roots by measuring the gradient of electrochemical potential of H^+ in the solution close to the root surface. The technique of microelectrode ion flux estimation has been used subsequently by many researchers to estimate H^+ fluxes at the surface of roots [27–38].

The development of ion-selective microelectrodes was pioneered by Walker [39] and Thomas [40] in the 1970s. A microelectrode consists of an ion-selective liquid membrane enclosed in a fine glass capillary. The liquid membrane must be
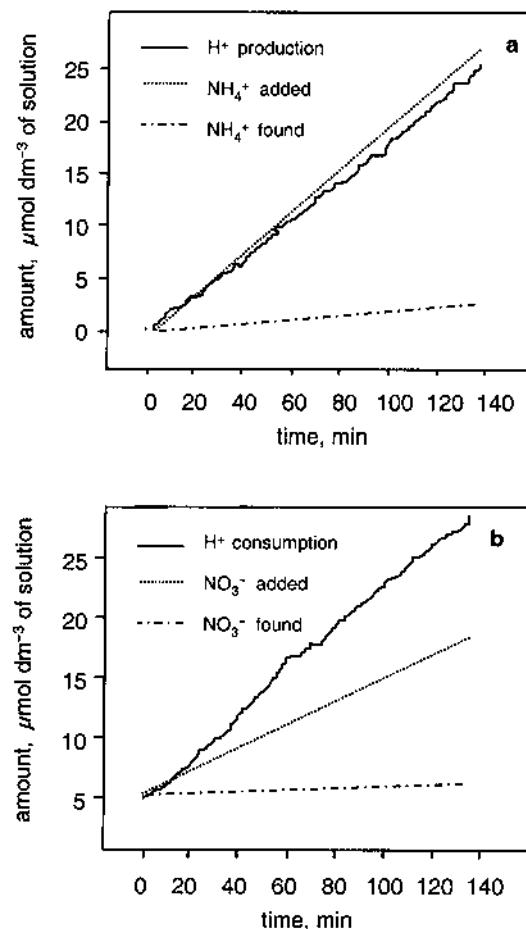
FIGURE 1 Stoichiometry of H^+/NH_4^+ (a) and H^+/NO_3^- (b) exchanges by corn. The data were measured by titrimetry using a pH-stat system. (Redrawn from Ref. 25. Copyright 1997, Blackwell Science Ltd, UK.)

hydrophobic to separate the internal reference phase from the solution to be measured. It is therefore necessary to make the inner side of the glass capillary hydrophobic. This is carried out by silanization, the quality of which determines the electrode performance [41,42]. The electrode selectivity depends upon the nature of the liquid membrane, generally called a cocktail. Today, many different ready-for-use cocktails are commercially available and make it possible to design microelectrodes that are selective for several ions: H^+, Na^+, K^+, or Ca^{2+}. The activities of other ions such as NO_3^- and NH_4^+ can be measured with mixtures that

must be prepared by the operator. After silanization of the glass capillary, its tip is filled with less than 1 μL of the selective membrane before back-filling the capillary with a saline solution containing the ion to be measured. Intact electrodes have a tip diameter smaller than 1 μm and a resistance in the order of 10^{10} Ω. Breaking the tip decreases its resistance and the response time of the electrode; a tip 5 μm in diameter gives good performance. Because of this high resistance, an electrometer with very high input resistance (at least 10^{14} Ω) is required [32] and the whole measuring device must be insulated by and grounded to a Faraday cage.

2.2.2   Principle of Ion Flux Determination

Root geometry may be approximated by a cylinder with ion flux presumably occurring in the radial direction only [43]. This hypothesis leads to expressing ion flux by a simple relation between concentration and distance to the geometrical axis according to the equation

$$J = \frac{2\pi D(C_2 - C_1)}{\ln(R_2/R_1)} \tag{2}$$

where J is the ion net flux per unit length of root, D is the self-diffusion coefficient of the studied ion, and C_1 and C_2 are its concentration at the two radial distances R_1 and R_2 from the geometrical axis of the root [27,29,30]. Experimentally, the hypothesis of a cylindrical geometry for roots can be checked by measuring ion concentrations at various distances from the root axis (Fig. 2). The concentrations in solution are calculated according to Nernst's law:

$$C = \exp\left(\frac{\mu - \mu_0}{RT}\right) \tag{3}$$

where μ and μ_0 are the sample and standard electrochemical potentials of the studied ion, R the constant of perfect gases, and T the absolute temperature. Microelectrodes are calibrated in standard pH solutions in order to calculate the Nernstian slope, which generally varies between 56 and 58 mV per logarithmic unit of concentration.

The main error in the flux calculation is due to the error in positioning the microelectrodes relative to the root axis, especially for fine roots [43]. Indeed, one of the trickiest steps of this method is to measure accurately the root diameter and the radial distance of the microelectrode from the root surface. This must be carried out under microscope magnification using a calibrated eyepiece reticle [43,44] or a computer-controlled motor-driven translation stage [38]. The positioning of microelectrodes in the unstirred layer can be achieved by moving the microelectrode itself by using a motor-driven micromanipulator that supports the microelectrode holder [27,30,32,43,44] or the root under study. In the latter case, the cuvette containing the root is placed on top of a computer-controlled motor-driven translation stage allowing vertical movements with micrometric precision [38].
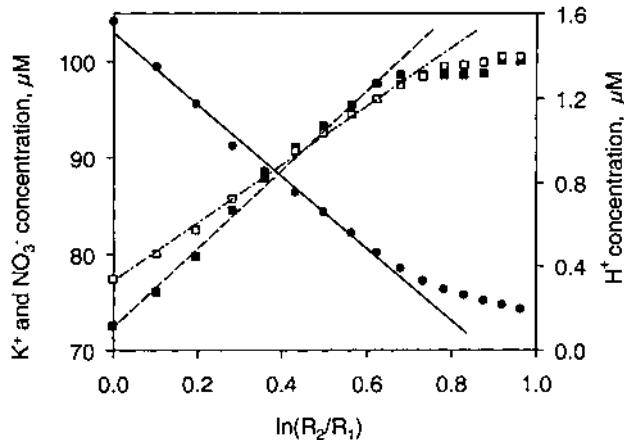
FIGURE 2 Profile of K$^+$ (■), NO$_3^-$ (□), and H$^+$ (•) activities as a function of ln(R_2/R_1), where R_1 is the radius of the root and R_2 the distance to the root axis, for a primary root of corn. The data were measured using ion-selective glass microelectrodes. (Redrawn from Ref. 38. Copyright 1999, Kluwer Academic Publishers, Netherlands; and from Plassard, unpublished).

As previously pointed out, the observed H$^+$ fluxes can be different from the actual ones due to the buffering capacity of the solution. This problem was addressed from a theoretical point of view [45]. Regarding the utilization of buffered solution, it is possible to calculate the protonated buffer flux from the measured H$^+$ flux in solution. However, unbuffered solutions always have the buffering effects of water itself and more so of carbonates due to CO$_2$ dissolved from the atmosphere. The calculations demonstrated that in such solutions at pH 6.0 the flux carried by water and carbonates is about 1% of the measured H$^+$ flux. However, as previously mentioned [18], respiratory CO$_2$ produced by the root itself can have an important buffering effect, especially at pH higher than 6.0. Until now, this respiratory effect has never been taken into account, but this problem undoubtedly deserves further attention.

2.2.3 Coupling the Measurement of H$^+$ Fluxes and Ion Uptake Along the Roots

The microelectrode technique allows direct, noninvasive measurements of ion fluxes between tissues and the surrounding solution. These measurements are instantaneous and have a high spatial resolution due to the small size of the microelectrode tip, making it possible to identify differences in root activity over short distances (Fig. 3). In addition, ion fluxes can be measured at low external ion concentrations, generally in the micromolar range. H$^+$ and K$^+$ microelectrodes were
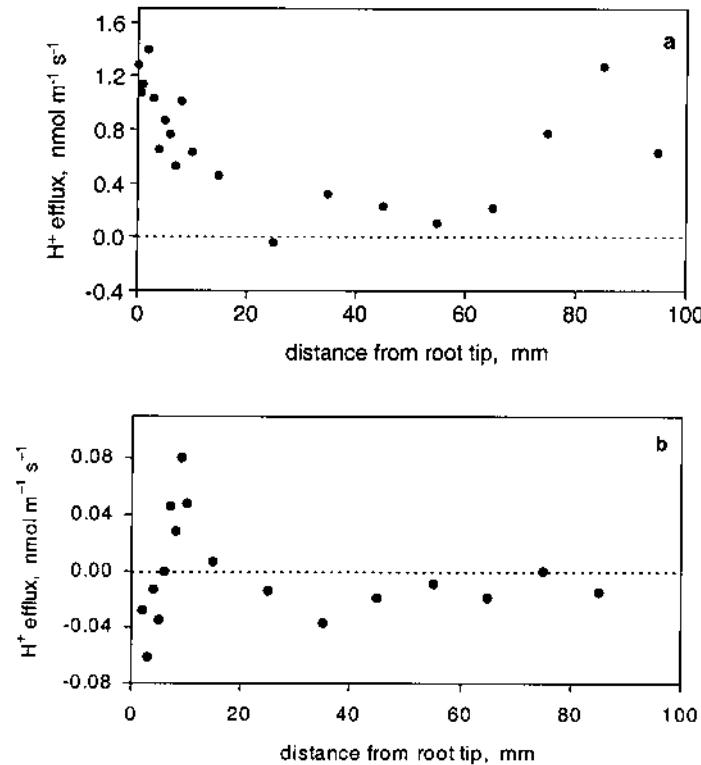
FIGURE 3 Profile of H^+ efflux along a primary root of corn supplied with NH_4^+ (a) or NO_3^- (b). The data were measured using pH glass microelectrodes. (Redrawn from Ref. 38. Copyright 1999, Kluwer Academic Publishers, Netherlands).

used to study the coupling between both ions, especially when external K^+ was supplied at low concentration (in the micromolar range). The hypothesis was that K^+ uptake is coupled, either directly or electrophoretically, to H^+ efflux. However, experimental data [27,28] from simultaneous measurements of fluxes did not support either form of coupling. In addition, the measurements of membrane potential carried out simultaneously during K^+ uptake suggested that K^+ influx occurred via a highly electrogenic process [27]. It was hypothesized that, at low K^+ concentration, K^+ uptake might be mediated by a K^+/H^+ cotransport system instead of an antiport one. This hypothesis was finally confirmed using a molecular approach [46].

Another coupling extensively studied with ion-selective microelectrodes was the coupling between H^+ and NO_3^-. Although it was established that nitrate

uptake leads to alkalinization of the nutrient solution, it was not clear whether NO_3^- uptake occurred via on H^+/NO_3^- symport or an OH^-/NO_3^- antiport. This question was especially studied with corn roots. The first results showed that nitrate uptake resulted in a strong membrane hyperpolarization and was not associated with an increase in the inorganic carbon efflux, strongly suggesting the operation of an OH^-/NO_3^- antiport [47]. Further study of the effect of NO_3^- uptake on membrane depolarization revealed that a transient depolarization was occurring before the hyperpolarization [48]. It was concluded that the depolarization was due to the operation of an H^+/NO_3^- symport and that the subsequent hyperpolarization resulted from the stimulation of the plasma membrane, occurring secondarily from the operation of the H^+/NO_3^- symport. Finally, the authors concluded that their data provided evidence for the operation of an H^+/NO_3^- symport with a stoichiometry that differed from the unity [30]. A comparison of H^+ fluxes determined along corn roots using selective microelectrodes after growth with NH_4^+ or NO_3^- confirmed the low values of H^+ fluxes in the presence of NO_3^- in the solution [38,49].

In addition, ion-selective microelectrodes made it possible to investigate the early consequences of different stresses applied to roots, such as wounding [31,50], osmotic or temperature stresses [34,35], and Al toxicity [51,52]. For instance, a concentration of 10 μM Al^{3+} inhibited both the net H^+ current and root growth of an Al-sensitive wheat cultivar within only a few hours, whereas no change in either current magnitude or root growth was observed with an Al-tolerant wheat cultivar [51]. Measurements with ion-selective microelectrodes demonstrated that H^+ influx was responsible for most of the current at the root tip, with smaller contributions from Ca^{2+} and Cl^- fluxes.

2.2.4 Limits and Advantages of the Microelectrode Ion Flux Estimation

The microelectrode technique enables noninvasive measurements of ion fluxes in space and time and appears to be a promising tool to study local variations in H^+ fluxes as a function of various factors. These can consist of physical or chemical treatments applied to the plant before or during the measurements, such as using nutrient solutions containing various ionic concentrations or composition. Although this method has been used in herbaceous species, it should also be convenient to determine H^+ fluxes along heterogeneous root systems, such as those of woody plants.

The method, however, has some limits. The major limitation is related to the possible errors in flux calculation as previously discussed. A second one is related to the variability of fluxes that have been observed in some cases. However, this problem can be minimized by using a flowing nutrient solution during the experiment [38]. Another limitation is represented by the time required to carry out one scan, restricting the possibility of scanning a whole root system, contrary to other

methods, such as the agar-indicator method (see Sec. 2.3). Finally, the intensity of the fluxes can be too low to be measurable with microelectrodes. However, this can be solved by using a vibrating ion-selective microelectrode system that has better sensitivity than conventional microelectrodes [29].

2.3 Local Measurements by Colorimetry

2.3.1 A Simple Method to Monitor pH Changes Induced by Roots in Their Environment

The staining reactions of dye indicators have been used in chemistry, biology, and geology for a long time. They make it possible to follow the progress of chemical reactions and to identify the nature of specific components or the location of tissues or minerals. These methods are based upon the change in optical properties of molecules according to their chemical status or the formation or disappearance of colored substances. They are generally rapid and easy to use but qualitative rather than quantitative. In physiology and soil–root interaction studies, they have been used mainly for monitoring reduction and acid–base reactions or activity of compounds such as enzymes [53–56].

The use of dye indicators to reveal and locate the activity of H^+ release by roots was proposed by Weisenseel, Dorn, and Jaffe in 1979 [57]. These authors were studying the steady electric currents around growing plant cells such as pollen tubes or root cells. These endogenous currents occurring around roots of higher plants had been known for many years and had raised many questions [58]. Using the vibrating probe technique, which is based on the measurement of the voltage difference between the two points of vibration probe positioning [59,60], Weisenseel et al. [57,61] showed that the electric currents entered at the level of the growing parts of pollen tubes, root apices, and root hairs and left out the other parts of cells or roots. Using bromocresol purple, a pH dye indicator, included in an agar sheet to visualize H^+ dynamics around roots, these authors showed that the electric currents corresponded mainly to H^+ fluxes around the root cells and root hairs. The pH around the apical and basal zones of roots and the basal zone of root hairs increased, showing inward H^+ flux, whereas pH strongly decreased along the elongation zone of roots and at the tip of root hairs, showing outward H^+ flux.

This work was important for several reasons. First, it confirmed that, with plants as with animals, the electric and electrogenic processes play a fundamental role in cell growth. Their location, direction, and intensity determine the growth of an isolated cell as well as the development of plant organs. Second, it established the relationship between endogenous electric currents and H^+ fluxes. The electric currents that had been studied for many years in plants were mainly supported by fluxes of H^+. With roots, the charge fluxes were induced by ion exchange activity between the root and its environment. Finally, these authors rein-

troduced an old but simple and effective method for monitoring these charge fluxes, to locate them, to determine their direction, and to estimate their intensity. Since then, this method has been adopted by many authors and has yielded important results on root growth and exchange activity.

2.3.2 Growth, Geotropism, and Electrogenic Activity of Roots

The following studies based on the preceding method had two main objectives. The first one, following the footsteps of Weisenseel et al. [57], was aimed at establishing the relationship between growth and electrogenic activity of roots. The ultimate objective was to verify the hypothesis of acid growth [62–64]. This theory was based upon the fact that cell wall elongation was favored under acidic conditions. Therefore, it hypothesized that plants developed specific adaptations to acidify cell was where cells are growing. The electric currents being mainly supported by H$^+$ fluxes, it became easier and faster to measure directly these fluxes or their consequences in terms of pH change around the roots. Moreover, the color changes of a dye indicator made it possible to obtain, within a few minutes, an overall picture of the behavior of the whole root system.

Mulkey and Evans [65] studied the qualitative response of plants subjected to different stimuli in terms of direction of H$^+$ flux in different parts of plant roots embedded in an agar gel that contained a dye indicator [65,66]. Thereby, they showed that a growth inhibitor stopped the root elongation and the H$^+$ flux simultaneously. Also, the geotropism appeared as differential growth of the upper and lower sides of the root, which induced the gravicurvature of the root. At the same time, the upper side of the root that grew faster released much more H$^+$ than the lower side that grew more slowly [65]. These results were confirmed later by quantitative measurements with micropotentiometry [67].

Other authors have tried to quantify the color changes of a pH dye indicator. Pilet, Versel, and Mayor [68–70] focused their research on the topological and quantitative relationship between elongation and H$^+$ flux along the roots. The variation of elongation rate along the roots was measured using beads glued on the root surface whose positions were determined at different time intervals. The rate of H$^+$ release along the same roots was evaluated using these porous beads, which had been immersed in a solution containing the appropriate pH indicator. The color changes of the beads were then estimated visually by referring to a color standard scale that had been obtained independently in controlled conditions. This original and elegant work clearly demonstrated that the elongation rate of the root cells was closely related, in terms of location and intensity, with the H$^+$ flux released by roots. With corn, the H$^+$ efflux was maximal at about 3–4 mm from the root tip, where the cell elongation was also maximal [68]; the initial pH was 6.8, and the pH drop reached 1.8 pH units at the root surface. The intensity of the pH drop increased with root growth rate [69].

2.3.3   Environmental Conditions, Mineral Nutrition, and Charge Efflux from Roots

The second group of studies involving the agar-indicator method was aimed at evaluating the effect of environmental conditions on the mineral nutrition of plants and the charge flux consequently released by roots in their environment. The ultimate objectives were (1) from an ecological point of view, to improve our understanding of the adaptive responses of plants to different soil conditions, and (2) from a physiological point of view, to have a better understanding of the processes used by plants for modifying their immediate environment and, thereby, for mobilizing the mineral nutrients.

Marschner, Römheld, and coworkers have widely used and improved the method of pH dye indicators, and more generally several other methods of staining, for their ability to yield overall pictures of the behavior of the whole root system of plants in response to environmental conditions [55,56]. These authors have especially studied the diverse strategies that plants have developed for iron acquisition in soils. Iron is a poorly mobile element in most soils, especially when it occurs as Fe^{III} (oxidized state). Plants have developed several mechanisms to increase Fe^{III} solubility, transport, and uptake (e.g., reducing activity, release of H^+, organic anions, and phytosiderophores by roots [71,72]). Previous results showed that root tips exerted specific chemical actions, among which H^+ release has a strong effect on Fe mobility. The staining methods were well adapted to demonstrate, locate, and estimate the intensity of root actions. For this purpose, Römheld and Marschner have been using several indicators included in agar films: (1) a red-colored chelate of Fe^{II} for demonstrating Fe reducing activity, (2) a brown precipitate of MnO_2 for showing Mn reducing activity, and (3) bromocresol purple for detecting H^+ release by roots [73]. The results obtained with these three visual methods were very demonstrative. They showed that, in dicots, the iron deficiency enhanced the reduction of Fe^{III} in the medium and the release of H^+ by roots (Fig. 4). These processes were generally located around the root tips, where changes in cell structure were also reported [74].

The agar-dye indicator method also contributed to elucidating the cation–anion balance in plants and the direction of charge fluxes that were exchanged between roots and soils according to different environmental constraints: nitrogen nutrition [8,75,76], nature of ions [75], mineral nutrient deficiencies such as Fe or P [73,76,77], plant species [74,78], or symbiotic status of legumes [8]. Generally speaking, these studies underlined the ecological significance of (1) the direction and the intensity of charge flux released by roots and the induced pH changes in the rhizosphere, which significantly modify the root environment and the mobility of mineral nutrients, and (2) the location of H^+ extrusion in certain zones of roots, thus concentrating H^+ in small volumes of rhizosphere and increasing the efficiency of roots in mobilizing soil mineral nutrients.
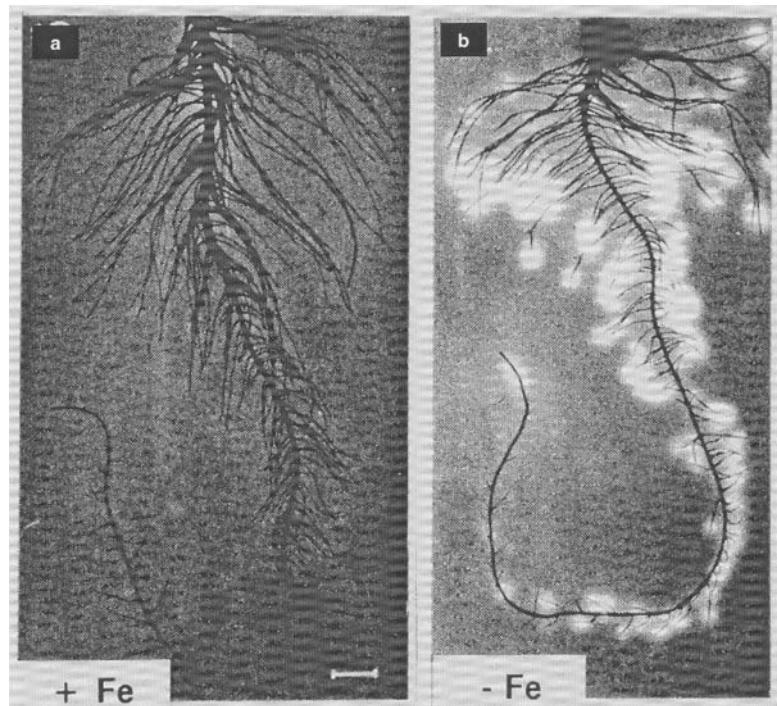
FIGURE 4 Effect of Fe deficiency on H$^+$ release by sunflower roots. Images with (a) and without (b) Fe supply were obtained using a pH dye indicator technique. The white zones indicate local acidification of the medium to pH 5.0 and lower. (From Ref. 8. Copyright 1984, American Society of Plant Physiologists, USA).

2.3.4 Principle, Advantages, and Limitations of the Agar-Indicator Method

The agar-indicator method has been generally used as a qualitative method. Very few workers have tried to quantify this color-based information [68,70,71,79,80]. It is nonetheless a classical colorimetric method that can be easily used for quantitative purposes by using a spectrodensitometer [77,81]. Only three indicators have been selected and used because they do not have any harmful effect on the growth and exchange activity of roots: bromocresol green, bromocresol purple, and phenol red. It has, however, been reported that the phenol red reduced the growth of barley roots [57]. These three indicators are sulfonphthaleins acting as weak acids in water, with pK values of 4.7, 6.4, and 7.8, respectively [81]. The

color change results from a shift in the equilibrium between only two forms, phenolic and quinonic. We can thus write

$$AH \Leftrightarrow A^- + H^+ \tag{4}$$

with

$$K = \frac{[A^-][H^+]}{[AH]} \tag{5}$$

or

$$K = \frac{(1-x)}{x[H^+]} \tag{6}$$

where K is the dissociation constant of the indicator, and x is the molar fraction of the indicator in acidic form, $x = [AH]/([A^-] + [AH])$. The optical density of the solution (D) is determined by the proportion of each form present at any given wavelength for a given concentration of indicator, as shown by the relation

$$D = xD_A + (1-x)D_B \tag{7}$$

where D_A and D_B are, respectively, the optical densities of the acidic and alkaline solution [82]. By combining Eqs. (6) and (7), we can write

$$[H^+] = \frac{K(D - D_B)}{(D_A - D)} \tag{8}$$

then

$$pH = pK + \frac{\log(D - D_A)}{(D_B - D)} \tag{9}$$

This relation leads to using acidic and alkaline standard agar sheets as calibrating references for D_A and D_B. It is important that the thickness of the agar sheets is constant on the whole analyzed area (for applying the Beer–Lambert law). To facilitate the measurement, the pH of the agar sheet can be mapped directly using a scanning video camera connected to a computer for calculation and image analysis [82] (Fig. 5). The pH images can then be converted into images of total H^+ concentration in the medium, knowing its H^+ buffering capacity according to Eq. (1). The H^+ fluxes along roots are then calculated as the differences in total H^+ concentrations at different time intervals [13,38] (Fig. 5). Videodensitometry is in good agreement with other methods such as micropotentiometry [38].

 The main advantages of the agar-indicator method are its simplicity and its ability to determine at once the response of the whole root system of a plant. It has
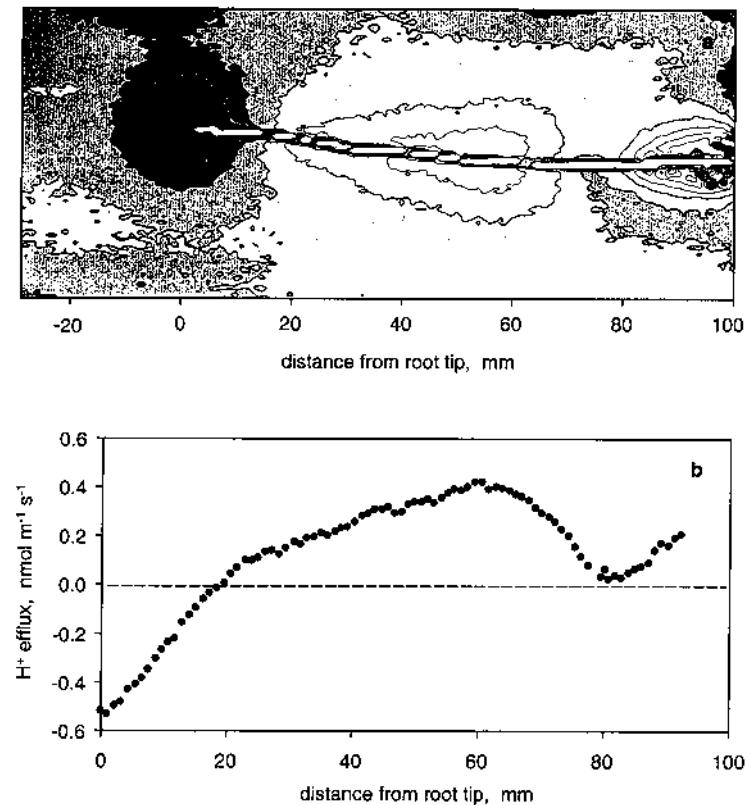
FIGURE 5 pH map (a) and profile of H$^+$ efflux (b) along a primary root of corn grown at pH 4.6. The data were measured by videodensitometry of a pH dye indicator. (a) White zones indicate local acidification, dark zones local alkalinization. The gray level changes each 0.05 pH units. (Redrawn from Ref. 82. Copyright 1996, Kluwer Academic Publishers, Netherlands).

often been used for prospective studies or in addition to other methods that are more time consuming or more sensitive but local, such as micropotentiometry. The major limitation is the necessary transparency of the medium for valuable quantification. However, the agar-indicator method remains a convenient method to explore diverse plant species or genotypes or environmental conditions and surely the most didactic method to demonstrate the chemical actions that plant roots exert on their environment.

3 MEASUREMENTS OF H$^+$ CONCENTRATIONS IN THE RHIZOSPHERE

3.1 Sampling of Rhizosphere Soil and Solution

3.1.1 The Straightforward Root-Shaking Approach: Sampling the Soil Adhering to the Roots

The simplest technique for collecting rhizosphere soil samples was first described and used by Riley and Barber [83]. To our knowledge, it was the first convincing report of significant pH changes occurring in the rhizosphere. At plant harvest, these authors carefully separated the roots plus adhering soil from the bulk of the soil. They discarded the portion of soil that was weakly adhering to the roots (as removed by gentle shaking) and considered as rhizosphere ("rhizoplane") soil the portion that was strongly adhering to the roots (and roughly 0 to 2 mm from the root surface). The soil pH was then measured in a conventional way for both types of samples. They applied this technique successfully to show significant pH changes occurring in the rhizosphere of soybean (*Glycine max* L.) in relation to the form of nitrogen supplied. This technique has been applied for sampling rhizosphere and bulk soil in both pot and field experiments for crops [83–85], trees [86–89], and other wild plants [90]. Several of these studies showed significant changes of pH occurring in the rhizosphere relative to the bulk soil.

A major limitation of this rather straightforward approach is the possibly poor representativeness of the so-called rhizosphere or rhizoplane soil. Indeed, the method of separation of rhizosphere and nonrhizosphere soil provides an operational but rather arbitrary distinction. The amount of soil strongly adhering to the roots indeed depends much on physical properties of the interface such as soil texture, humidity, concentration of mucilage, or root hairs, i.e., properties that may vary with soil type, plant species, root type or root portion, etc. It should also be stressed that sampling the rhizosphere soil adhering to fine roots is even harder. In addition, the spatial extension of the rhizosphere in terms of pH change is likely to be different (larger or smaller) from the spatial extension of the strong adhesion that roots can exert to soil particles, leading to biased results. When this technique is directly applied in situ, especially for natural ecosystems, another major difficulty is to make a clear distinction between a true rhizosphere effect and artifacts due to the initial heterogeneity of the soil that plant roots may exploit when colonizing the soil [90]. The results obtained with this technique thus need to be interpreted cautiously, particularly when applied to undisturbed soil (for in situ measurements).

3.1.2 The Root Mat Approaches

An alternative technique for sampling rhizosphere soil is derived from the early work of Farr et al. [91], who first grew a dense, planar mat of roots against a volume of soil that was ultimately sliced parallel to the mat of roots in order to col-

lect soil samples at various distances from the roots. These authors showed a marked depletion of K ions and an increase in H$^+$ concentrations in the vicinity of the roots of onions (*Allium cepa* L.). The technique was further refined by Kuchenbuch and Jungk [92], who inserted a nylon mesh between the roots and the soil to avoid penetration of the roots into the soil during the experiment [93]. Such a technique and its many derivatives, sometimes called rhizoboxes, were successfully used by many authors to show significant changes in pH occurring near plant roots and to determine the spatial extension of these rhizosphere processes [93–99]. With this approach, significant changes in pH of up to more than one pH unit were demonstrated to occur and extend over one to several millimeters, with a typical H$^+$ diffusion pattern (Fig. 6).

However, this technique has been criticized because of the unrealistic (planar) geometry of the rhizosphere it provides and because of the subsequent risks of overestimating the intensity and spatial extension of rhizosphere processes compared with a radial geometry [100]. In addition, the soil slicing procedure is tedious and needs to be achieved as quickly as possible after the removal of the root mat to avoid a redistribution of ions, including H$^+$/OH$^-$, during the procedure [93]. To avoid the need to slice a soil column and to compare large numbers of treatments and/or replicates, the technique can be simplified by using a thin layer of soil (2 to 3 mm) in contact with the mat of roots [101–103]; this soil layer could be considered the rhizosphere soil, based on the spatial extension of rhizo-
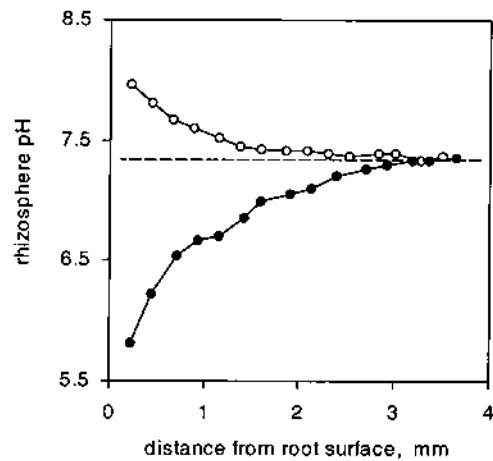
FIGURE 6 Profiles of pH in the rhizosphere of ryegrass grown in a luvisol and supplied with NH$_4^+$ (•) or NO$_3^-$ (○). The data were obtained using the root mat approach. (Redrawn from Ref. 96. Copyright 1992, Kluwer Academic Publishers, Netherlands).

sphere processes as previously reported in the literature. This technique can illustrate significant pH changes occurring in the rhizosphere, relative to unplanted pots of similar geometry and incubated in a similar manner [103]. Another approach in which plant roots are grown directly in the thin layer of soil sandwiched between two glass slides is based on similar basic assumptions: once a sufficient density of roots have colonized the soil, the whole of it can be considered the rhizosphere [104]. This experimental device that is easy to set up and handle was successfully used to show dynamics of rhizosphere pH [105,106].

3.1.3 Approaches Designed for Sampling Defined Root Zones

All the previously described approaches are destructive in essence. They enable collection of large amounts of rhizosphere soil for making soil pH measurements in a usual manner (with a conventional electrode) and even simultaneously carrying out other measurements of physicochemical or biological properties of the rhizosphere. This is, however, achieved by bulking up the rhizosphere material collected for the whole root system of a single plant or a group of plants. Therefore, another major limitation of these approaches is that they do not give access to the spatial heterogeneity of pH changes that are known to occur along the root system (see Secs. 2.3.2 and 2.3.3). To assess this spatial variability, several authors have used rhizotrons that allow visualization of the distribution of the root system at the soil surface and collection of small samples of rhizosphere soil around given portions of the root system [107–109]. However, these procedures are tedious and their reproducibility on a large scale is rather questionable. In addition, given the small amounts of soil that can be collected in that way, microprocedures of sampling and analysis needed to be designed. For instance, an immiscible displacement–centrifugation technique was proposed to enable the collection of the soil solution from rhizosphere soil samples of less than 6 [107].

Göttlein et al. [110,111] proposed an alternative approach to collecting small volumes of soil solution at defined locations along the root system. This technique was based on the use of an array of microsuction cups that were inserted in the vicinity of roots grown in rhizotrons (Fig. 7). It enabled the measurement of the pH and ionic concentrations in small volumes of soil solutions that were collected at various time intervals during plant growth by applying suction to the microsamplers [110–112]. This approach therefore provides a unique, nondestructive method for sampling the rhizosphere soil solution and for measuring the pH changes at defined locations along the root system.

3.2   Use of pH Dye Indicators in the Rhizosphere

The simplicity of using the agar-indicator technique described in Sec. 2.3 has led several authors to adapt it to field conditions for convenient estimation of the root-
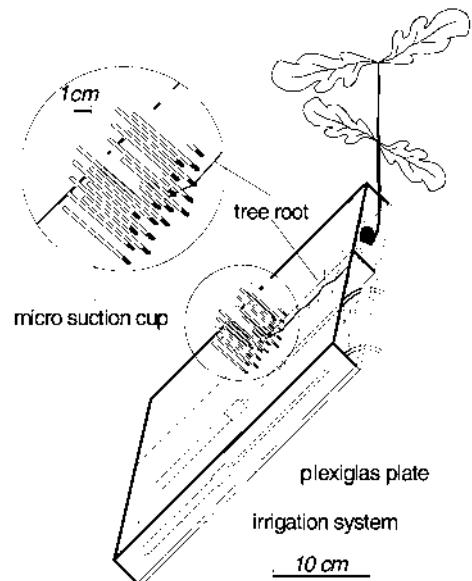
FIGURE 7 Experimental device for sampling the soil solution in the rhizosphere of a tree seedling with an array of microsuction cups. (Redrawn from Ref. 110. Copyright 1996, Elsevier Science, Ireland).

induced pH changes under natural conditions [113–122]. However, the principle of the technique has considerably limited such developments. This approach was initiated by Marschner and Römheld [113]. It was based on using an agar film that included the pH indicator to obtain the pH map in the rhizosphere in a manner similar to the use of a photographic film in autoradiography. Plants were grown in rhizotrons that were slightly inclined so that roots preferentially grew against the front glass slide. Thin agar sheets that included the indicator were molded and cooled separately. For measuring the rhizosphere pH, the front glass slide of the rhizotron was removed and replaced by the agar sheet. The H$^+$ diffused from the soil solution into the agar sheet, causing a change in the color of the indicator and hence revealing the rhizosphere pH within a few minutes. The method produced valuable results when the pH changes were large enough to induce consequent color contrasts. The results were dependent on the type of soil used, light-colored soils being more suitable than dark ones.

The agar-indicator technique has been used especially by authors who studied the release of H$^+$ by tree roots because these roots are too rigid to be laid onto an agar sheet, as opposed to roots of herbaceous plants. The use of a premolded agar sheet laid onto roots grown against a glass slide made it possi-

ble to overcome such experimental difficulties. Häussling et al. [114] and Marschner et al. [115] were thereby able to study the behavior of roots of 4-year-old Norway spruce (*Picea abies* L. Karst.) grown in pot experiments as well as those of a 60-year-old Norway spruce grown in a forest stand. These data are among those obtained with the oldest plants grown in natural conditions. Studying the nitrogen nutrition of Douglas fir (*Pseudotsuga menziesii*) and the consequent H^+ release by roots, Gijsman [86,121] simplified the procedure by using only small strips of agar to cover given portions of the roots from place to place. The principle remained the same: aiming to explore the root behavior in situ in field conditions. It should be stressed that the use of the agar-indicator technique was combined with local measurements of pH using microelectrodes [114–121]. The microelectrodes were carefully inserted into the agar sheet in the rhizosphere soil or in the immediate vicinity of root surface. The agar sheet provided a moist environment in the rhizosphere and prevented the drying out of both soil and roots during the course of the measurement, thereby improving the reliability of the pH values obtained.

All the previous studies were achieved in very acid soils whose bulk pH was below 5.0 or even 4.0. In such conditions, it appeared that pH near the root surface increased at the root tips and decreased farther away from the tip relative to the bulk soil pH. The pH increased especially when nitrogen was supplied as nitrate. The reported pH changes were substantial in such acidic conditions and might have contributed to modifying significantly the physicochemical dynamics of elements such as aluminum or the microbial activity in the rhizosphere. However, the results obtained with this method remained qualitative in essence, and only the combined use of quantitative techniques such as pH microelectrodes made it possible to assess the actual pH values in the rhizosphere.

3.3   Use of pH Microelectrodes in the Rhizosphere

The most direct method for measuring H^+ activity is potentiometry (see Sec. 2.2). However, few scientists have been using this method for measuring rhizosphere pH because of the experimental difficulties encountered in the soil and especially in situ in field conditions. In fact, soil is a medium that is definitely not suitable for using fine probes such as pH microelectrodes. First of all, it is opaque, which raises the problem of properly positioning the probe. Either blind positioning of probes or rather destructive positioning of the probes is needed to access the most relevant sites. In addition, sturdy probes are needed to penetrate into the soil because of mechanical constraints. Finally, soil is a rather dry medium, which raises the problem of liquid continuity between the probe and the soil. These reasons explain why only a few scientists used potentiometry for measuring the rhizosphere pH, but they nevertheless produced some remarkable results.

3.3.1   The Criticized but Sturdy Antimony Microelectrodes

A major step forward in using microelectrodes for measuring rhizosphere pH has
been accomplished by Schaller and Fischer [123–128], who underlined that glass
electrodes were unsuitable for long-term pH measurements in microsites in soil
because of their shape and size and because of the drying of the glass membrane
[123]. They therefore developed microelectrodes based on antimony oxidoreduc-
tion in water, which can be described by the following equations [123,129]:

$$Sb_{(s)} \Leftrightarrow Sb^{3+}_{(1)} + 3e^- \tag{10}$$

and

$$Sb_2O_{3(s)} + 6H^+ + 6e^- \Leftrightarrow 2Sb_{(s)} + 3H_2O_{(1)} \tag{11}$$

Combining these two redox half-reactions (10) and (11), the result is

$$Sb_2O_{3(s)} + 6H^+ \Leftrightarrow 2Sb^{3+}_{(1)} + 3H_2O_{(1)} \tag{12}$$
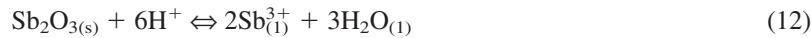
Because they are based on a solid surface reaction, the electrical impedance of an-
timony microelectrodes is lower than that of glass electrodes; therefore, their tip
may be easier to miniaturize. Moreover, they are sturdy, easy to build, and may be
used conveniently in a wide range of conditions. Microelectrodes were con-
structed by sucking melted antimony into preheated glass capillary tubes less than
1 mm in diameter [114–116,123–126]. After cooling, the antimony bar was ex-
truded and fastened in a Pasteur pipette that had been formerly insulated with wa-
terproof plastic. Finer tips were obtained by melting together antimony and a glass
capillary that had been especially selected for its melting temperature [130].

This simple and cheap method for building antimony microelectrodes has
made it possible to produce a large number of them. Fischer et al. [128] con-
structed regular arrays of microelectrodes inserted in rhizotrons to monitor the
root-induced pH changes in the rhizosphere of growing roots (such as the device
showed in Fig. 7). The quantitative data obtained in these experiments that were
conducted over several days in different soils confirmed numerous previous ob-
servations made with plants cultivated in hydroponics and also pointed out the pe-
culiar role the soil played in rhizosphere pH changes. They showed, for instance,
that the root activity of groundnut (*Arachis hypogea* L.) and consequent pH
change in the rhizosphere develop cyclically according to a diurnal cycle: in a
loam soil at pH 5.0, the rhizosphere pH fluctuated between 5.0 and 3.5–3.8, de-
pending on the exposure of plants to light. With the same plant species grown in
a brown soil at pH 5.5 fertilized with NH_4^+, the pH values in the rhizosphere de-
creased to less than 3.0 within a single day [124]. When investigating the positions
of the electrodes relative to the root tip, it was confirmed that the pH change was
maximum between 1 and 3 cm behind the tip (a drop of up to 2.5 pH units), with
an average decrease of around 2.0 pH units along the mature parts of the roots

[124]. In an alkaline soil at pH 7.8, rhizosphere pH decreased with NH_4^+ and increased with NO_3^- supply, but the intensities of pH changes were much lower than those mentioned previously for an acid soil because of the large buffering capacity of the alkaline soil. In very acid soils at pH 3.2, rhizosphere pH increased up to 4.0 within 1 day, as reported for tree roots grown in natural conditions and fed with nitrate [86,114,121].

The same experimental device using an antimony microelectrode array also made it possible to evaluate the effect of H^+ released by roots in determining the extent of spatial extension of pH changes in the rhizosphere in terms of the radial distance from roots [124–127] (Fig. 8). The H^+ buffering capacity of soils is generally higher than that of soil solution because of the ability of the soil solid phase to react with H^+ (1) via cation exchange reactions, (2) via protonation/deprotonation of weak acid groups on soil constituents, and (3) via dissolution or precipitation of soil minerals (reactions that respectively consume or produce H^+). Schaller and Fischer [126] showed that, after acid addition, the H^+ activity in soil solution steeply increased first, then slightly decreased for several hours before reaching equilibrium. Investigating the influence of soil pH buffering on the extension of rhizosphere pH changes, Schaller [127] showed that the pH change induced by roots was strongly and linearly correlated with the short-term buffering capacity of the soils as determined 5 minutes after acid addition (when measured in soil suspensions). This suggested that the pH profile around roots, and thus the
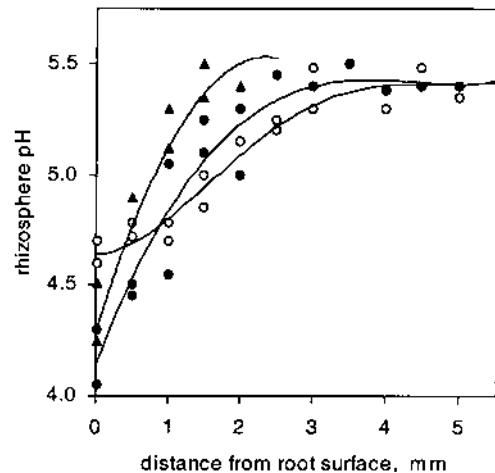
FIGURE 8 Profiles of pH as a function of the distance from the surface of a single root of groundnut grown in rhizotron. The data were measured after 20 (▲), 30 (•), and 60 hours (○) using antimony microelectrodes. (Redrawn from Ref. 124. Copyright 1985, Wiley-VCH, USA).

extension of pH changes in the rhizosphere, resulted from dynamic interactions between continuous H$^+$ release by the growing roots and H$^+$ uptake by the buffering solid phase of the rhizosphere. In the studied soils, the extension of pH changes in the rhizosphere of groundnut was 2 mm on average: it was largest in soils with an initial pH of 5.5 (2.8 mm) and smallest (1.4 mm) in more alkaline and acidic soils, which was in good agreement with theory [6].

Fischer and Schaller [131] had formerly built an array of platinum microelectrodes for measuring redox potential in the rhizosphere. Using combined arrays of antimony and platinum microelectrodes (matrices made of 30 to 50 electrodes), these authors [128] successfully measured simultaneous changes in pH and redox potential in the rhizosphere of faba bean (*Vicia faba* L.) They thereby monitored the evolution of rhizosphere pH and Eh over time periods of 3 to 4 days (Fig. 9). Measurements near a growing root showed a rapid drop of both pH and Eh for about 1.4 pH units and 330 mV, respectively. Changes in redox potential and pH are not independent; indeed, a reduction process is expected to be accompanied by a pH increase [5], whereas a net pH decrease was reported in the present case. This pH change can be explained to a large extent by the cation–anion balance at the root–soil interface, whereas the decrease in redox potential was attributed either to root and microbial respiration or to the exudation of reducing compounds by plant roots [128].

Antimony microelectrodes have severe limitations that restrict their practical use to defined experimental conditions. The main limitation is their sensitivity to several environmental factors, such as the concentrations of oxygen and carbon dioxide and those of organic anions such as citrate or oxalate. For instance, in controlled conditions, the measured pH increases when pO$_2$ decreases [123] or citrate concentration increases [123,129]. On the one hand, the interference with oxygen results from the possibility to form a range of antimony oxides other than the main trioxide, which ultimately influences the electrode potential for a given H$^+$ concentration in solution. On the other hand, carbon dioxide and organic anions may form some complexes at the surface of the solid and also influence the electrode potential. In addition, the pH measured with the antimony microelectrode decreases with decreasing soil water content, and glass electrode measurements do not detect any change in soil pH [123,132]. All these environmental factors are likely to vary strongly in the rhizosphere [3]. The use of antimony microelectrodes therefore requires much caution to obtain reliable pH measurements. These microelectrodes should thus be kept only for experiments in controlled and steady-state conditions.

3.3.2 The pH-Sensitive Glass Microelectrodes

The glass membrane electrodes are undoubtedly the most selective and sensitive probes to measure the H$^+$ activity in soil and solution. Unfortunately, they have numerous limitations for use in soil conditions: (1) their large electrical
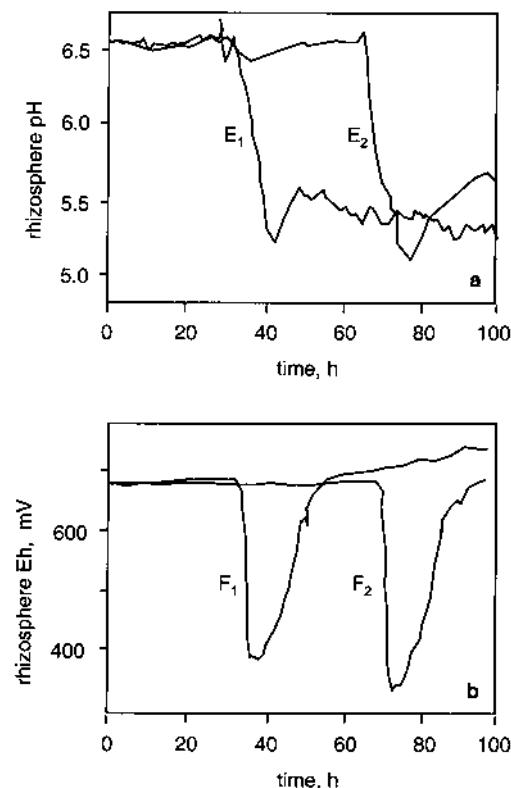
FIGURE 9 Evolution of pH (a) and Eh (b) at different positions in the rhizosphere of faba bean over several days of growth. The data were obtained using a grid of antimony (for pH) and platinum (for Eh) microelectrodes. The changes in pH and Eh occurred when the growing root approached the microelectrodes. The antimony microelectrodes E_1 and E_2 were near the platinum microelectrodes F_1 and F_2, respectively. (Redrawn from Ref. 128. Copyright 1989, Wiley-VCH, USA).

impedance requiring a large membrane area, (2) the necessity to prevent the glass membrane from drying, and (3) their particularly frustrating fragility. As previously pointed out, glass microelectrodes have, however, been occasionally used to complement other methods, such as the agar-indicator technique in soil [86,121,133]. However, the glass membranes of the electrodes used in these studies were about 2 mm in diameter, which makes them inappropriate for local measurements in the rhizosphere.

In the meantime, plant and animal physiologists have been developing liquid and glass membrane microelectrodes with tips as small as 1 μm or even less (see Sec. 2.2). After having used antimony microelectrodes [129,134], Blanchar and coworkers [135,136] designed a novel generation of glass microelectrodes that were both sturdy enough to be used in soil conditions and thin enough to allow pH measurements in soil microsites, i.e., small enough relative to rhizosphere dimensions. The basic idea was to strengthen the sensing tip in order to stand moderate physical constraints without damage. The design was an inner insulated pipette inserted into a sealed pH-sensitive glass tip 10 to 20 μm in diameter, the whole lot being inserted in a glass support [135]. The microelectrode construction and calibration for pH measurements in soil were later improved [136]. Because of the sensitivity of microelectrodes to electrical interference, the entire measurement device needed to be insulated and grounded to a Faraday cage.

These pH-sensitive glass microelectrodes have been used for measuring pH in the rhizosphere of plants growing in different conditions [78,137,138]. For instance, Conkling et al. [137] studied the effect of acidity applied to the shoots of corn (*Zea mays* L.), alfalfa (*Medicago sativa* L.), and soybean (*Glycine max* L.) to simulate acid rains. Plants were grown in rhizotrons filled with acidic soil ranging in pH from 4.2 to 6.5. They showed that rhizosphere pH change was linked to acidification (except for alfalfa grown at pH 5.5). Moreover, the reported pH drop increased with the initial bulk pH: with corn it was nil at pH 4.0 and reached on average 0.75 pH units at pH 6.0, and with soybean it was also nil at pH 4.0 and reached 1.35 pH units at pH 6.0. In spite of the poor nodulation of soybean roots, soybean decreased the rhizosphere pH to a greater extent than corn. In addition, the pH change was greater near neutrality than in acidic conditions, which was in good agreement with theory [6]. It should be borne in mind, however, that pH 4 is already a very acidic pH for plants.

These results were confirmed by measuring the rhizosphere pH of field-grown soybean [138] (Fig. 10). The prime objective was to evaluate the influence of the thickness of the soil surface horizon on root growth and rhizosphere pH. Soil–root cores were sampled in the field, frozen, and brought back to the laboratory for further measurements. They were then thawed and dissected carefully to display the roots and surrounding soil. Soil pH was measured with a glass microelectrode at 0.5 and 5 mm from the root surface, the sensing tip (20 μm in diameter) being inserted to a depth of about 100 μm into the soil. This procedure was repeated at three time intervals. The method of freezing and thawing of the soil–root cores might be criticized because of the potential artifacts it could have generated by inducing a release of the root cell content, for instance. However, the results obtained with this method were consistent and in agreement with other studies. They showed that pH in the rhizosphere of soybean was always lower than bulk soil pH. The pH change was correlated with the initial pH of the bulk soil: almost nil for a bulk pH of 4.0 and increasing (in absolute value) with increasing
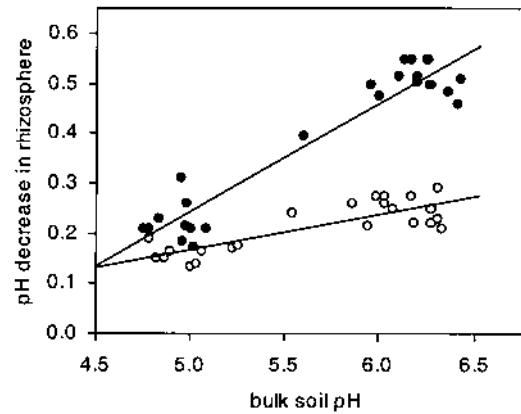
FIGURE 10 Changes of pH in the rhizosphere of lateral (•) and primary (○) roots of soybean after 55 days of growth in field conditions versus bulk soil pH. The data were measured in the laboratory using pH glass microelectrodes. Bulk soil pH was the pH of soil at 5 mm from the root surface. (Redrawn from Ref. 138. Copyright 1996, Soil Science Society of America Inc., via Copyright Clearance Center, USA).

bulk pH (Fig. 10). This result is consistent with the data obtained using antimony microelectrodes [127] and with the theory, which shows that the buffering capacity of a soil solution is lower near neutrality [6]. In addition, these results showed that, for a given sampling time, the pH values in the rhizosphere of lateral roots were lower than those in the rhizosphere of the primary roots (Fig. 10). Above all, following several field studies [85,88–90,114,116], this work definitively demonstrated that the pH around roots of field-grown plants can be significantly different from the bulk soil pH. This should be taken into account for better understanding plant growth and plant nutrition in soils in the field.

The use of pH-sensitive glass microelectrodes is restricted because they are not commercially available and require technical expertise to be properly built. In addition, the mechanical fragility of the sensing tips is a major limitation for their use. The results presented here showed that this difficulty can be overcome. More data should therefore be obtained with this technique in the future, in particular from in situ measurements of rhizosphere pH in field conditions. Generally speaking, the potentiometric methods may potentially give access to other significant soil parameters such as specific ion activities. The technique of microelectrodes based on a glass membrane or liquid membrane consolidated with polyvinyl chloride [139], which has already been considerably improved, is likely to lead to further advances in this area. These microelectrodes should help to make another step

forward in the measurement of physicochemical conditions and associated fluxes of ions in the rhizosphere and other soil microsites.

4 CONCLUSIONS

Plant-induced pH changes were reported in the 19th century. In his treatise on agricultural chemistry, Dehérain [140] reported an experiment conducted by Sachs in 1860 that demonstrated that rootlets can secrete an acid powerful enough to dissolve calcium carbonate; this experiment was reproduced later by other authors [141], who showed etched traces of roots grown on the surface of a marble plate. In addition, in 1894, when designing a method for measuring plant available phosphorus, Dyer [142] selected citric acid as an extractant that would best mimic the acids supposedly produced by roots. However, these root-induced processes were then ignored for a long time, and almost nothing dealing with root-induced pH changes is to be found again in the literature prior to the 1970s.

Considerable progress has been achieved since the 19th century, and mostly over the last two decades, through the development of a range of techniques for measuring the fluxes of H$^+$ released by roots and the resulting rhizosphere pH. The most remarkable achievements have been obtained in vitro, in rather artificial, controlled conditions. The development of techniques such as pH-stat systems and micropotentiometry designed for solution culture experiments has helped ascertain the physiological origins of root-induced pH changes (e.g., root elongation, mineral nutrition, cation–anion balance, responses to environmental stresses such as wounding, deficiencies, or toxicities). The use of dye indicators has also helped provide evidence for the functioning of different parts of the whole root system of a single plant. In natural conditions, the available data on pH changes induced by roots in situ are, however, much less numerous, mostly because of lack of appropriate methods.

In acid soils, root-induced pH changes are of prime importance. Indeed, aluminum is a toxic element that severely limits growth at pH below 5.0 as a consequence of its pH-dependent speciation and the considerable increase in the solubility of aluminum-bearing minerals with decreasing pH. Under such acidic conditions, a further decrease in rhizosphere pH would lead to root intoxication by Al and impairment of plant growth. Several authors [13,143–147] have shown that the tolerance to soil acidity and Al toxicity in certain species or genotypes was related to their ability to take up H$^+$ and thereby to increase rhizosphere pH. Better knowledge of the H$^+$ fluxes in and out of roots in acid soils in field conditions might improve our understanding of plant adaptation to such adverse environments. Knowing their intensity, direction, and location along the roots and understanding the factors that determine these fluxes would provide the base to improve plant growth in acid soils.

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10

Toxic Elements in Acid Soils: Chemistry and Measurement

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1 INTRODUCTION

Soils are identified as being "acid" by their low pH, although H^+ per se is rarely the limitation to plant growth. Jenny [1] perceived that, during the 25 years that preceded his review in 1961, soil acidity research had come full-circle, from the identification by Veitch [2] that acid clays were Al clays to the 1960s interest in solution chemistry and exchange behavior of Al. Jenny felt that agronomists, who had once thought that plants in an acid soil were confronted by H^+ ions, had received a new stimulus with the recognition of Al toxicity as a limitation to plant growth in acid soils. He conjectured that "Presumably the plants knew this all along." Forty years after Jenny's review, the challenge to soil researchers remains the same, namely to identify which of the many potential effects of soil acidity is limiting plant growth.

Acid soil infertility is a complex interaction of growth-limiting factors. Plant growth may be restricted by one or more of the following: low pH; Al or Mn toxicity; Ca, Mg, P, or Mo deficiency; and reduced mineralization, nitrification, nodulation, and mycorrhizal infection [3]. Such effects are not confined to surface soils. Subsoil acidity may adversely affect plant growth, persistence through restricted depth of root proliferation, and nutrient and water uptake. This chapter

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deals primarily with the phytotoxic elements H, Mn, and Al. It addresses the effects of these toxic elements on plant growth, where appropriate the specific form of the element that is toxic, and the use of soil tests to identify situations in which these elements will limit plant growth.

2 SOIL PH

2.1 The Phytotoxicity of H$^+$

In soil culture, the direct assessment of the effects of H$^+$ is precluded by the confounding effects of Al and/or Mn released by mineral dissolution at low pH. However, studies conducted in solution culture have clearly demonstrated that H$^+$ can limit plant growth. Islam et al. [4] observed root injury in six crop species at pH 3.3 and pH 4.0 but not at pH 4.8. Blamey et al. [5] reported within-species differences in response to H$^+$ for sunflower (*Helianthus annuus* L.), with critical solution pH (90% maximum total dry matter yield) for four cultivars ranging from pH 3.9 to pH 4.5. A solution pH of 3.5 was found to be lethal to all four cultivars tested. Excess H$^+$ ions have a marked effect on membrane structure and function. Foy [3] cited examples of reduced uptake of Ca, Mg, Mn, Zn, Cu, and P and loss of organic substances and nutrient ions by H$^+$-damaged roots. Although H$^+$ is directly detrimental to plants, in low pH mineral soils the adverse effects of Al and/or Mn toxicity generally considerably outweigh the adverse effect of H$^+$.

2.2 Measurement of pH

Soil pH is regarded as a controlling variable in soil systems, influencing ion exchange, solubility, adsorption, redox, and complexation reactions. It is undoubtedly the measurement most commonly made on soils. Measurements of soil pH are generally made by determining the electrical potential difference between a glass membrane electrode, which is responsive to H$^+$ activity, and a reference electrode that generates a known and constant potential. The electrical circuit is completed through a salt bridge that permits ions to diffuse from the internal solution of the reference electrode to the external solution. The selection of an appropriate salt for the internal solution in the reference electrode is critical, as an unbalanced diffusion of anions and cations across the salt bridge would produce a junction potential. Concentrated KCl is typically used as a reference electrode filling solution as K$^+$ and Cl$^-$ have almost identical mobilities; thus, the junction potential should be small [6]. In soil suspensions, the effects of charged colloids on the mobility of ions disrupt this ideal behavior, leading to the development of higher junction potentials in soil suspensions than in clear solutions. Published procedures for pH determination differ widely in their treatment of this issue, with methods recommending placement of the glass electrode and salt bridge in the supernatant, placement of the glass electrode in the suspension and salt bridge in the

supernatant, and measurement in a constantly stirred solution. The critical issue is that the measurements be made in a consistent way [7].

The pH of soil suspension is influenced by the ratio of soil to solution, with 1:1, 1:2, and 1:5 ratios all commonly used. In soil suspensions the pH is buffered by dissociation of H^+ from the soil surface and hydrolysis of Al [7], maintaining a relatively stable pH with dilution. Nevertheless, the amount of hydrolyzable acidity is finite and the pH tends to increase as the suspension is diluted. Furthermore, dilution reduces the displacement of Al^{3+} and H^+ by soluble salt cations, contributing to the increase in measured pH with dilution.

The pH is also dependent on the salt content of the measuring solution. A criticism of pH measured in deionized water suspensions is that seasonal change in a soil's soluble salt content or the addition of neutral salt fertilizers can lead to changes in the measured pH. The measurement of pH in salt solutions such as 0.01 M $CaCl_2$ or 1 M KCl has been advocated to suppress this effect [8]. However, this approach confounds explicit acidity (proton or active) with latent acidity (proton generating or reserve). Furthermore, the use of salt solutions will mask the "real" pH changes that can result from the addition of neutral salts. The impact of neutral salts on soil acidity is well demonstrated by the reduced soil solution pH and increased Al toxicity that can result from the application of gypsum to soils [9].

The use of a concentrated salt solution to measure pH results in displacement of Al^{3+} and H^+ from exchange sites and the deprotonation of variable charge sites on organic matter and mineral surfaces. Thus, the suspension pH will be artificially lowered. In contrast, an unequivocal estimate of active acidity is provided by a measurement of soil solution pH. This is the pH condition encountered by plant roots and that at which reactions occur in the soil. Thus, the most appropriate medium for measuring soil pH would be one that best simulates the characteristics of the soil solution [10]. Gillman [11] suggested that measurement at an ionic strength of 0.005 M would be appropriate for tropical soils on the basis of the low ionic strength of their soil solution. The effectiveness of pH measurement in a dilute salt solution was demonstrated for 90 soils from eastern Queensland by Aitken and Moody [12], with a 1:5 soil/0.002 M $CaCl_2$ suspension providing the closest approximation to the soil solution pH.

3 MANGANESE

3.1 Manganese as a Plant Toxin

Manganese is an element essential for plant growth, but it becomes detrimental when the supply to the plant is excessive. Manganese is readily taken up and transported from roots to shoots [13]. This probably accounts for the early appearance

of Mn toxicity symptoms on shoots. It is generally accepted that Mn(II) is the prevailing source of Mn for plant uptake. Critical Mn concentrations in the range of 0.2 to 12 mM have been reported to produce severe growth limitations in solution culture studies of species such as cotton (*Gossypium hirsutum* L.) [14], sweet potato (*Ipomoea batatas* L.) [15], sorghum (*Sorghum bicolor*) [16], and wheat (*Triticum aestivum* L.) [17]. In contrast to these studies conducted in high-ionic-strength solutions, critical values one to two orders of magnitude lower have been obtained from low-ionic-strength systems more representative of conditions in soil solutions [18]. Dilute flowing solution culture studies have shown that critical external Mn(II) concentrations for toxicity (90% maximum whole plant yield) vary widely among plant species, with wheat and corn (*Zea mays* L.) relatively sensitive (critical concentration 1.4 μM) and sunflower particularly tolerant (critical concentration 65 μM) [19]. For cowpea (*Vigna unguiculata* L.), Taylor et al. [20] observed toxicity symptoms at 0.5 μM Mn, with a 25% reduction in growth at 1.0 μM Mn.

Despite the use of solution conditions comparable to soil solution, direct translation of solution culture values to soil culture is precluded by the capacity of plants to alter conditions within their rhizosphere. Certain Mn-tolerant varieties of wheat, barley (*Hordeum vulgare* L.), rice (*Oryza sativa* L.), peas (*Pisum sativum* L.), and corn increase the pH of their rhizosphere [21], decreasing the Mn availability. The superior Mn tolerance of rice over soybean (*Glycine max* Merr.) is attributed to the capacity of rice roots to oxidize Mn from the soluble divalent to relatively insoluble trivalent form, decreasing uptake by the plant [22]. Doi [22] found that soybean was injured by Mn if planted alone in paddy soils, but the extent of injury was reduced if rice was planted with soybean. The beneficial effect was probably due to the decreased soil solution Mn(II) concentration as a result of Mn oxidation and precipitation in the rice rhizosphere. In contrast, to the oxidizing nature of the rice roots, conditions in the rhizosphere of most plants are likely to favor the reduction of Mn to the soluble divalent form [23]. The plant's influence on the rhizosphere means that the condition of the bulk soil may provide a poor indication of the Mn concentration at the root surface.

Expression of Mn toxicity is markedly affected by the supply of other nutrients. A protective effect of Si has been widely reported, although the means by which this effect is mediated is not clear [24]. The severity of Mn toxicity is inversely related to the supply of Ca and Mg, and both positive and negative interactions with the supply of Fe have been reported [24]. Plants supplied with N as NO_3^- develop Mn toxicity symptoms and have higher tissue Mn concentrations than plants supplied with NH_4^+ [25,26]. Plants supplied with NO_3^- tend to raise the pH of their rhizosphere [27], decreasing the solubility of Mn; thus, the increased Mn uptake where NO_3^- is supplied is clearly not the result of N supply–induced rhizosphere pH change.

3.2 Solution Chemistry of Mn

Manganese (II) is the only oxidation state of Mn expected in appreciable concentrations in solution within the pH and pe ranges found in soils [28]. Higher oxidation state Mn(III) and Mn(IV) are considered too reactive to persist in soil solution, although Mn(III) may be present as an intermediate in soil redox reactions [29]. Complexing ligands can stabilize Mn(III) in solution temporarily, but disproportionation of Mn(III), oxidative decomposition of the associated ligand, and low solubility of Mn(III) and Mn(IV) oxides limit the persistence of Mn(III) complexes in solution [29].

Fully hydrated Mn^{2+} is the dominant inorganic Mn species in soil solutions and natural waters. Ion pairs with SO_4^{2-}, HCO_3^-, and Cl^- are formed but would be present only at activities equal to that of Mn^{2+} where the anions are present at activities of 0.005, 0.016, and 0.25 M, respectively [28]. Of the three anions, only sulfate is likely to be encountered in acid soils at activities of this magnitude [18].

Complexation of Mn(II) by a range of organic ligands is possible [30]; however, the stabilities of Mn(II) complexes are too low for Mn^{2+} to compete effectively with relatively abundant cations such as Ca^{2+} and Mg^{2+} [30]. This prediction has generally been supported by studies of soil solution composition. In an acid sandy loam soil, Sanders [31] found that organic complexation of Mn increased from 10% as the pH was raised by liming, reaching a maximum of 65% above pH 7. In six flooded soils, Olomu et al. [32] found that 25 to 40% of soil solution Mn was retained by an anion exchange resin, whereas 100% was retained by a cation exchange resin, suggesting that some form of labile, organically bound Mn was present. In marked contrast to these studies, Geering et al. [33] reported organic complexation of 84 to 99% of the Mn in the soil solutions from 13 topsoils of widely differing pH and texture.

3.3 Identification of Mn-Toxic Soils

Whereas the form of Mn available to plants is well known and is readily quantified by routine analytical methods, the accurate determination of the concentration of Mn to which plant roots are exposed remains problematic. This arises in part from the effects of roots on conditions in their rhizosphere but is also the result of the complex behavior of Mn in soil systems. The simplest representation of Mn reactions in soil can be given as [34]

$$\text{Root} \xleftarrow{\text{Uptake}} Mn^{2+} \xrightleftharpoons[\text{Red.}]{\text{Ox.}} MnO_x$$
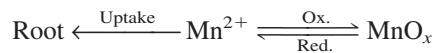
where Mn^{2+} can be oxidized by soil microorganisms to insoluble oxides MnO_x (where $1 < x < 2$). Even in aerobic soils, MnO_x is continuously being reduced to Mn^{2+} by soil organic matter. The balance between these reactions in soil is one of quasi-equilibrium because the forward and reverse reactions are somewhat inde-

pendent of one another and may be separated spatially. At any point in time, the concentration of water-soluble plus exchangeable Mn is determined by the relative rates of oxidation and reduction [34]. This complex field condition can easily be disturbed by soil sampling procedures and is drastically altered by air drying the soil [35].

Various extractants have been used to assess soil Mn, with dilute extractants generally found to be most effective. Water extracts (1:2 and 1:5) have been correlated with the growth of lespedeza (*Lespedeza striata* Thunb.), King Island meliot (*Melilotus* sp. Mill.) [36], and kikuyu (*Pennisetum clandestinum*) [37] and found to be more effective than measures of exchangeable Mn or reducible Mn in predicting Mn toxicity in cotton [38]. Extraction with 0.01 M $CaCl_2$ was a more effective predictor of Mn uptake by barley, turnip rape (*Brassica campestris* L.), alfalfa (*Medicago sativa* L.) [39], subterranean clover (*Trifolium subterraneum* L.), and switchgrass (*Panicum virgatum*) [40] than methods intended to assess acid-soluble, exchangeable, or reducible Mn [40,41].

Soil solution Mn concentration has been strongly correlated with plant Mn uptake in studies in which solution was extracted directly from field-moist soil [40,42,43]. However, where soil was air dried and then rewet prior to soil solution extraction, the effectiveness of soil solution Mn concentration as a predictor of plant Mn uptake was low [44]. In a study of Mn uptake by rice in acid sulfate soils, Moore and Patrick [42] found plant uptake of Mn more closely correlated with p(Mn/Fe) than with Mn^{2+} activity, confirming the Mn/Fe interaction reported in solution culture experiments [24].

Soil testing to identify Mn toxicity has not been widely adopted, and few critical values have been published. Hoyt and Nyborg [41] proposed the use of 0.01 M $CaCl_2$ as an extractant for Mn and subsequently refined the extraction procedure [45,46] but did not report critical values. The Hoyt and Nyborg extractant, 0.01 M $CaCl_2$, is increasingly being adopted as a test for Mn toxicity and a number of critical values have been published: rape (*Brassica napus* L.) > 20 mg kg^{-1}, subterranean clover >50 mg kg^{-1} [44], poppy (*Papaver somniferum*) two sites >5.1 and >0.5 mg kg^{-1} [47], barley, wheat, and triticale (*Triticum* $\times$ *Secale*) <10 mg kg^{-1} nonlimiting [48]. Direct comparison of these critical values is precluded by the wide variation in sample treatment between studies; some samples were analyzed in the field-moist state while others were air-dried or oven-dried at 40°C. These differences in sample treatment will alter the Mn chemistry of the sample and change the soil test critical value obtained [35].

Additional difficulties in establishing critical values for Mn toxicity arise from the confounding effects of Al toxicity in acid soils. This effect was well demonstrated by the data of Hoyt and Nyborg [45], who found that for 40 acid soils, the Mn content of a 0.02 M $CaCl_2$ extract was strongly correlated with Mn uptake by barley, rape, and alfalfa (correlation coefficients of 0.75, 0.84, and 0.83, respectively) but poorly correlated with plant yield (partial regression coefficients

of -0.12, -0.45, and -0.07, respectively). The Al concentration of the same extract was more strongly correlated with yield, giving partial regression coefficients of -0.87 for barley, -0.45 for rape, and -0.61 for alfalfa. As Al toxicity is likely to be encountered in many acid soils with Mn toxicity problems, accurate prediction of plant growth limitations is likely to require the determination of both elements. As a general rule, Mn toxicity alone may be encountered between pH 5.5 and 5.0, and both Mn and Al toxicity may be encountered below pH 5.0.

3.4 Manganese Determination

Manganese is readily determined at trace levels by a range of analytical techniques. Flame atomic absorption spectrometry (AAS) can determine Mn at concentrations in the range 0.1 to 10 mg L^{-1}, with an instrument detection limit of 0.01 mg L^{-1} [49]. Interferences in the determination can be overcome using a combination of boric acid and strontium chloride (500 mg L^{-1} each) [50]. Sensitivity can be improved by a liquid–liquid preconcentration extraction into a solution of 8-hydroxyquinoline in chloroform [51], by on-line preconcentration and solvent elution of diethyldithiocarbamate Mn complexes [52], or by adsorption of the Mn complexes with cupferron on activated carbon. The detection limit of the latter method is 1.8 µg L^{-1} [53]. Greater sensitivity can be achieved using electrothermal excitation [54], with transverse heating and longitudinal Zeeman effect background correction systems achieving a detection limit of 0.026 µg L^{-1} [55].

The simultaneous, multielement capabilities of inductively coupled plasma atomic emission spectroscopy (ICP-AES) have been widely exploited in the analysis of biological materials. The approach has a detection limit of 2 µg L^{-1} for Mn [49] and has been used with preconcentration to improve sensitivity [52].

A range of colorimetric methods is used for the determination of Mn in waters. The most commonly used approach is based on the oxidation of Mn(II) by persulfate in the presence of silver nitrate to form the permanganate anion [49]. Flow analysis using this approach produced a linear response from 2.5 to 40 mg L^{-1} Mn(II) and a detection limit of 1.2 mg L^{-1} (99.7% confidence level) [56]. Recently developed chromogens are capable of measuring Mn(II) at much lower concentrations. The chromogenic system TCMOPPH2-Cd(II)-imidazole, using the novel synthetic chromogenic reagent meso-tetra[4-(carboxymethylenoxy)-phenyl]porphyrin (TCMOPPH2), achieved a linear range from 0.01 to 1.75 mg L^{-1} with a detection limit of 2.8 µg L^{-1} [57], and oxidation of Mn(II) in a strong basic medium and colorimetric determination using 3,3′,5,5′-tetramethylbenzidine yielded a detection limit of 3 µg L^{-1} [58].

Sensitive spectrophotometric determination of Mn(II) can be achieved by exploiting its catalytic effect on reactions. The catalytic effect of Mn(II) on the oxidation of diphenylcarbazone (DFC) in the presence of triethanolamine (TEA) has been employed for plant digests, achieving reproducible results in the concentra-

tion range 0.10 to 0.80 mg L^{-1} and a detection limit of 0.03 mg L^{-1} [59]. More sensitive procedures based on Mn(II) catalytic effects have been developed. A procedure based on the oxidation of 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) with periodate permits measurement of Mn in the concentration range 0.05 to 1.0 μg L^{-1} and produced a relative standard deviation (RSD) ($n = 10$) of 1.6% at 0.5 μg L^{-1} [60]. Other Mn(II) catalytic approaches include a reduced phenolphthalein-periodate reaction (linear range 2–200 μg L^{-1}, detection limit 0.9 μg L^{-1}) [61] and decomposition of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (NANA) with hydrogen peroxide (range 0.2 to 1 μg L^{-1}, detection limit 0.06 μg L^{-1}) [62].

4 ALUMINUM

4.1 Aluminum as a Plant Toxin

Although Al toxicity is recognized as the most common limitation to plant growth on acid soils, there are no identifiable symptoms of Al toxicity suitable for use as a diagnostic indicator [3], the most apparent effects being a reduction in both root and shoot growth. Typically, roots are more affected by Al toxicity than shoots. In plants exposed to high Al levels, elongation of the main axis is inhibited, and roots become thickened, stubby, brown, brittle, and occasionally necrotic [3].

Wood et al. [63] reported a critical Al^{3+} concentration for root elongation in white clover (*Trifolium repens* L.) of 30 μM, and the critical concentration for root hair formation was 10 μM. Hecht-Buchholz et al. [64] showed a limitation of root hair formation at a summed activity of Al monomers of 2.5 μM, and 12 μM completely inhibited root hair formation. Thus, microscopic effects on plant growth may occur at Al levels that do not affect the macroscopic appearance of the plant.

4.2 Solution Chemistry of Al

The chemistry of Al in aqueous systems is complex (even when relatively simple systems are considered) and has been the subject of considerable research (see reviews by Ritchie [10] and Sposito [65]). Aluminum entering solution coordinates with six water molecules that undergo hydrolysis to an extent determined by the solution pH (Table 1) [28]. Hydrolysis reactions are important at pH >4.0; >80% of the total Al is hydrolyzed at pH 4.9. As the extent of hydrolysis increases, the charge density of the Al molecule decreases and polymerization of Al units can occur. A diverse range of polymeric Al forms has been proposed, but the mechanism of their formation is not well understood. The amount and type of polymer formed may be influenced by the pH and Al concentration of the initial solution, the rate and extent of neutralization, the mixing conditions, and the time of aging [66]. Bertsch and Parker [66] considered that, of all the polymeric Al forms pro-

TABLE 1 Equilibrium Reactions of Al Complexes at 25°C

Equilibrium reaction	log $K^{\circ a}$
Hydrolysis	
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	-5.00
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	10.1
$Al^{3+} + 3H_2O = Al(OH)_3^\circ + 3H^+$	16.8
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	22.99
Other complexes	
$Al^{3+} + F^- = AlF^{2+}$	7.0
$Al^{3+} + 2F^- = AlF_2^+$	12.7
$Al^{3+} + 3F^- = AlF_3^\circ$	16.8
$Al^{3+} + 4F^- = AlF_4^-$	19.4
$Al^{3+} + 5F^- = AlF_5^{2-}$	20.6
$Al^{3+} + 6F^- = AlF_6^{3-}$	20.6
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	3.5
$Al^{3+} + SO_4^{2-} = Al(SO_4)_2^-$	5.0
$Al^{3+} + H_2PO_4^- = AlH_2PO_4^{2+}$	≈ 3
$Al^{3+} + HPO_4^{2-} = AlHPO_4^+$	≈ 7
$Al^{3+} + 3NO_3^- = Al(NO_3)_3^\circ$	0.12^b

[a] Formation constants are the selected values of Nordstrom and May [69].
[b] Fomation constant from Lindsay and Walthall [70].

posed, those having the most convincing experimental support were $Al_2(OH)_2^{4+}$, $Al_8(OH)_{20}(H_2O)_x^{4+}$, the "gibbsite fragment" model forms, $Al_6(OH)_{12}(H_2O)_{12}^{6+}$ through $Al_{54}(OH)_{144}(H_2O)_{36}^{18+}$, and the $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ species. It is generally accepted that polymeric Al forms are metastable intermediates in the precipitation of $Al(OH)_3$ and that a partially neutralized Al solution at equilibrium will contain only monomeric species and the stable solid phase [67]. Although polymeric Al forms may persist in pure solutions, they are unlikely to be important in soil solution given their high charge [66] and therefore high affinity for negatively charged soil surfaces. Brown and Hem [68] equilibrated synthetic Al solutions with various types of mineral surfaces and found that particulates rapidly facilitate the removal of polymeric Al. These solutions quickly reached an apparent equilibrium with respect to amorphous $Al(OH)_3$. In soil systems, the removal of polymeric Al forms would be further enhanced by the presence of flocculation-causing anions, such as phosphate, silicate, and sulfate [67].

In soil solution, complexation of Al by the inorganic anions SO_4^{2-}, F^-, and NO_3^- (Table 1) as well as by organic anions may occur. The activity of the $AlSO_4^+$ ion pair will exceed the activity of the Al^{3+} species only where free SO_4^{2-} activity

exceeds $10^{-3.2}$ M (0.63 mM), and SO_4^{2-} activities of 10^{-1} M (100 mM) would be necessary for the other Al-SO$_4$ ion pairs to become dominant [28]. Whereas SO_4^{2-} activities in excess of $10^{-3.2}$ M are unlikely to be encountered in virgin, highly weathered soils, they may be present following fertilization [71]. Similarly, F^- complexation of Al in virgin soils is likely to be low because soil solution F^- concentrations are usually $\leq 10^{-5}$ M [72,73]; however, Al-F pairs may be important where solution F^- levels are elevated in fertilized soils through the application of F^- present as an impurity in superphosphate [74]. Aluminum-NO$_3$ ion pairs will be of limited importance in soil solution as the affinity of Al for NO$_3$ is low [28].

Aluminum complexes formed with phosphate and silicate may also be important. Several authors have presented evidence for Al-OH-PO$_4$ polymers in dilute nutrient solutions at pH values from 4.1 to 4.8 [75–77]. Such forms were precipitated at higher pH values or increased concentrations. Silicate has been implicated in the solubilization of Al [78] and movement of Al through soil horizons [79].

In soil solution and natural waters, significant proportions of the soluble Al are present as complexes with organic ligands [80]. Aluminum complexation occurs predominantly with organic functional groups containing oxygen (COOH; phenolic-, enolic-, and aliphatic-OH groups; and possibly ketonic CBO and ester functional groups), whereas those containing nitrogen (amino acids and porphyrins) generally form weak complexes [81]. The relative importance of organic complexation in solution depends on the nature and concentration of the organic ligands, pH, ionic strength, and the kind and amount of competing cations. In a study of the stability of metal ion complexes with humic and fulvic acids, Schnitzer [82] found Al to be the second most stable complex; Fe complexes were more stable. A number of methods have been proposed to distinguish inorganic monomeric Al from organically complexed Al and polymeric Al forms. These are considered in the final section of this chapter.

4.3 Identification of Al-Toxic Soils

Measurements of the solid-phase characteristics of soils, such as pH, exchangeable Al, and Al saturation, have been widely used as diagnostic tools for the prediction of Al toxicity. Although critical values for such measures derived for a given crop on a given soil have generally provided a good prediction of plant performance, these predictors have not proved particularly useful when applied to a given species over a range of soils. Bell and Edwards [83] considered that the best relationships between plant growth and indices of Al availability would be found using soil solution parameters. Whereas studies in nutrient solution culture have shown that plant performance can be best predicted on the basis of the activity of monomeric Al in solution, attempts to relate plant performance to soil solution Al parameters have generally been unsuccessful. This may in part reflect our inabil-

ity to measure accurately the phytotoxic forms of Al present in soil solution. The following sections consider the various soil Al measurements used to assess soil acidity and their relative merits.

4.3.1 Solid-Phase Al

Exchangeable Al is the major reserve of labile Al and can readily enter the soil solution through exchange with other cations. The size of this reservoir is dependent on the cation exchange capacity (CEC) and the degree of Al saturation. For a given CEC, the amount of exchangeable Al is strongly pH dependent, decreasing with increasing pH to low levels at pH 5.5. Exchangeable Al is normally defined as the amount of the element extracted by an unbuffered neutral salt solution; 1 M KCl is most commonly employed, with the use of other salts producing slightly different results [84]. Whether this extracted Al is truly exchangeable is the subject of considerable debate. Aluminum extracted by 1 M KCl could include Al from precipitated or amorphous $Al(OH)_3$ [85] and disordered aluminosilicates, hydroxy-Al interlayers, or organic Al complexes [86]. Several authors have reported that Al activity in KCl extracts approached that supported by gibbsite dissolution [85,87], the cumulative amount of Al extracted being greater for concentrated extractants even after exhaustive leaching [88]. In response to the difficulties presented by neutral salt extraction, Kotze et al. [89] attempted to determine exchangeable Al by isotopic exchange with ^{28}Al. They found that, in some soils, isotopically exchangeable Al did not appear to be related to neutral salt exchangeable Al and concluded that isotopic exchange provided an improved means of studying exchange reactions of Al. However, the validity of this approach is questionable because exchange of ^{28}Al with Al atoms present as an integral part of soil minerals cannot be precluded.

Wada [90] proposed that, in ando soils where the soil pH is lower than the point of zero net charge, high-ionic-strength extractants caused adsorption of H^+ by variable charge surfaces resulting in an increase in extractant pH. This pH increase would result in precipitation of Al released from exchange sites on the soil, thus giving the impression of low exchangeable Al levels in such soils. In contrast, Gillman and Sumpter [91] concluded that for a range of highly weathered soils from north Queensland, Al extracted by 1 M KCl was exchangeable after finding that the extracted Al correlated well with the difference between measured CEC and the sum of exchangeable bases.

Exchangeable Al has been used as a criterion for the determination of lime requirement [92,93]. Such lime rate determinations require the application of an empirical factor to allow for the neutralization of acidity other than KCl-exchangeable Al; these multiplication factors vary widely, e.g., from the addition of Ca at 1.5 times the exchangeable Al level [92] to 6.5 times the exchangeable Al [94]. Numerous authors have employed salts other than KCl in an attempt to improve the prediction of lime requirement. The use of $CuCl_2$ has been advocated,

as the high affinity of Cu for organic sites will result in the release of organically complexed Al [95]. It is also considered to extract reactive interlayer Al [96]. Lime rates based on $CuCl_2$-extractable Al have been found to be excessive [97], as organically complexed Al does not contribute to titratable acidity [98]. The use of $LaCl_3$ has also been suggested, as its ability to extract Al is intermediate between those of KCl and $CuCl_2$ [99].

The degree of Al saturation of the CEC has been found to be a more successful predictor of Al toxicity than exchangeable Al [100]. For a given species on one soil or a group of similar soils, the increases in crop growth with increments of lime addition correlate well with reductions in Al saturation, but critical levels obtained from such studies are not quantitatively applicable to other soils [101]. Adams [102] and Kamprath [100] cite studies in which critical Al saturation values range from 5 to 25% for soybean growth, depending on the soil type studied. Similarly, Bruce [103] cites critical Al saturation values for corn ranging from 5 to 70% depending on soil type. Thus, Al saturation represents a poor predictor of Al toxicity over a range of soils.

In addition to representing a pool of reserve acidity, exchangeable Al occupies exchange sites that would otherwise be available to retain nutrient cations. This effect is accentuated by the reduction of the CEC of variable charge surfaces as pH decreases. Menzies and Gillman [104] considered that this loss of base cation retention capacity represents another facet of degradation resulting from soil acidification and proposed a degradation index (DI) capable of representing this form of soil quality deterioration.

$$ \text{DI}\,(\%) = \left(\frac{\text{CEC}_b}{\text{CEC}_{5.5}} \right) \times 100 $$

In this equation, CEC_b is the capacity of the soil to retain base cations at its field pH and $\text{CEC}_{5.5}$ the CEC at a pH of 5.5 as measured by the charge fingerprint method [105]. Use of $\text{CEC}_{5.5}$ was intended to provide an assessment of the soil's condition prior to acidification; the exchange is essentially free of Al, and the surface charge density increased by the increased pH. If the pH of the system prior to acidification were known, this pH could be used in place of pH 5.5

Extraction with 0.01 M $CaCl_2$ has been used to assess the potential for Al toxicity [39]. In contrast to the extraction of the total exchangeable Al pool by concentrated extractants (a capacity measurement), the use of 0.01 M $CaCl_2$ is intended to provide an indication of the Al concentration present in the soil solution (an intensity measure). This approach has been used in Australia with considerable success over a range of soil types and for numerous plant species [106].

4.3.2 Soil Solution Al

Adams and Lund [107], in a series of experiments investigating the effects of Al toxicity on cotton root elongation, found that reasonable prediction of Al toxicity

could be achieved if soil solution Al concentration were corrected to molar activities. They reported a critical Al activity (90% relative root length) of 1.5 μM for cotton in three subsoils. Their calculations assumed that all Al was present as Al^{3+}. Adams et al. [108] showed reduced root penetration into subsoils by cotton at <1 μM Al, and Adams and Pearson [109] found reduced peanut (*Arachis hypogaea* L.) root growth in subsoils at 9 μM Al^{3+} activity. Similarly, Richburg and Adams [110] found reduced penetration of cotton roots into three surface soils at 10 to 17 μM Al activity. Following calculations to account for hydrolysis reactions, critical Al activities of <2 μM were determined.

In contrast to the success of these early experiments, subsequent studies using the same approach have been less satisfactory [101,111]. Adams and Moore [112] and Adams and Hathcock [101] noted ambiguities in the relationship between plant growth and the Al level measured. Aluminum toxicity appeared in some soils with Al concentrations ranging from <0.4 to 14 μM, and the range for nontoxic horizons was <0.4 to 134 μM. Ranges of summed activities of Al^{3+}, $AlOH^{2+}$, and $Al(OH)_2^+$ were <0.3 to 10 μM and <0.3 to 98 μM for toxic and nontoxic horizons, respectively.

The inferiority of relationship between Al activity and plant growth derived from soil culture experiments, relative to those derived in carefully controlled solution culture studies, has generally been attributed to the inability of analytical procedures to discriminate inorganic monomeric Al forms from organically complexed Al [101,112,113]. An additional factor may be the influence of matrix effects in soil culture studies. Horst et al. [114] found that, in order to inhibit sorghum root growth to the same degree, a 10 times higher Al level was required in sand culture than in solution culture. They suggested that this discrepancy may be due to (1) slower movement of Al to the roots by diffusion in sand than by convection in aerated solution culture, (2) increased pH at the root surface leading to precipitation of Al, and (3) enhanced release of root exudates that complex Al. Although the experiment of Horst et al. [114] considers matrix effects that may occur in soil, Al supply is limited by mass flow of solution, or diffusion of Al, and the total concentration of Al in solution is fixed. In soil culture, additional Al can be released into solution by mineral dissolution or cation exchange. Furthermore, as these effects can take place in the immediate vicinity of the root, the plant's capacity to detoxify Al may be quickly overcome. Nevertheless, as matrix effects may be important, care should be taken in the comparison of critical values derived from solution and soil culture experiments.

Studies conducted in solution culture under carefully controlled conditions have demonstrated that the activity of Al in solution is a more accurate predictor of Al toxicity than Al concentration [111,115]; however, the relative toxicity of the individual ionic species remains unclear. A particular difficulty is presented by the monomeric hydrolysis species because several of these species coexist in solution; thus, individual species cannot be investigated in isolation. Furthermore,

the activities of individual species must be calculated from equilibrium data that may be uncertain [116]. It appears that Al^{3+} is toxic and the Al-OH pairs are less toxic or nontoxic [117].

Phytotoxicity of polynuclear Al has been demonstrated in culture solutions of simple chemical composition [118,119], with Parker et al. [120] identifying Al_{13} as the specific ion responsible. Toxicity of this species toward wheat is some 5 to 10 times greater than that of Al^{3+} when compared as concentrations of atomic Al in each form (a comparison based on moles of each molecular species would result in an even larger differential toxicity), with ≈ 3 μM Al as Al_{13} producing complete inhibition of root growth. Although conditions suitable for the formation of Al_{13} may occur in simple culture solutions, these polymers are unlikely to be encountered in soil systems.

Results of studies conducted in nutrient solution culture have indicated that Al ion pairs with SO_4^{2-} [121,122] and F^- [122,123] are nontoxic or less toxic than Al^{3+} or Al ion pairs with OH^-. The nontoxicity of $AlSO_4^+$ has also been indicated by soil culture experiments [9,113,124]. Ion pairs of Al with F appear to be toxic, although less so than Al^{3+}. Kinraide [117] concluded that the relative toxicity of Al ions to wheat roots was $Al_{13} > Al^{3+} > AlF_2^+ > AlF^{2+}$.

The nontoxicity of organically complexed Al has been suggested by nutrient solution culture studies in which the toxicity of Al was ameliorated by the addition of organic acids [118,125,126]. This conclusion has also been inferred from the observation that addition of organic matter to acid soils results in amelioration of Al toxicity [127]. However, more careful investigation of this amelioration has revealed that pH changes resulting from organic matter addition may be more important than complexation of Al [127,128]. The soil pH change that will result from an organic matter addition can be predicted from the basic cation content of the material [129].

Aluminum toxicity rarely occurs above pH 5.0. As the pH decreases below this value, the solubility of Al-containing minerals increases exponentially; thus, the probability of Al toxicity to plants becomes higher as pH decreases [70]. There appears to be no unique relationship between soil pH and solution Al [110], and pH has not proved to be a good indicator of Al toxicity [107]. Nevertheless, pH can be an effective predictor of Al toxicity across soils of similar mineralogy. In highly weathered soils, soil solution pH was an effective predictor of Al toxicity as assessed by root elongation [9,113,128]. In these soils, pH is an effective predictor of root growth inhibition because of its strong correlation with Al^{3+} activity; this relationship is attributed to the control of Al^{3+} activity by gibbsite dissolution [73,130]. Measurements of soil solution pH also account for root growth limitations attributable to H^+ ion toxicity.

Numerous studies have indicated that increasing concentrations of Ca can mitigate the adverse effects of Al on plant growth. This amelioration appears to result from the displacement of cell-surface Al by Ca-induced reduction in cell

surface negativity and to a lesser extent from the restoration of the cell surface to nonlimiting levels of Ca [131]. To accommodate specific ameliorative effects of Ca on Al toxicity, various Ca-Al activity ratios have been proposed as diagnostic indices of Al toxicity for crop and pasture species [111,132,133]. Ratios of soil solution Al to Ca have also been employed to assess the impact of soil acidity on deciduous and coniferous forests. Cronan and Grigal [134] concluded in their review of this research that "there is a 50:50 risk of adverse impacts on tree growth or nutrition when the soil solution Ca/Al ratio is as low as 1.0."

4.4   Aluminum Determination

Aluminum is generally present in solution in soils and natural waters at low concentrations [71,135]. Thus, with the exception of very acidic waters, analytical methods with detection limits of 0.5 μM or less are often needed [136]. This issue is accentuated in chromatographic methods requiring postcolumn Al quantification. The numerous forms of Al that may be present further complicate the situation. To identify accurately soils that present plants with an Al challenge, the analytical approach used must be able to discriminate between toxic and nontoxic forms of Al. This section considers methods used for the determination of total Al, with particular emphasis placed on errors caused by the presence of dissolved organic matter or particulate Al and on the determination of specific forms of Al in solution (speciation).

4.4.1   Atomic Absorption and Emission Spectroscopy

Flame atomic absorption spectroscopy (flame AAS) has limited sensitivity for Al even with the use of the N_2O/C_2H_2 flame (optimum range 5 to 100 mg L^{-1}), due to the formation of refractory oxides [49]. Although the low sensitivity of this technique prevents its direct use on natural water samples, effective measurement of Al has been achieved with flame AAS using a prior extraction and concentration into a nonaqueous solvent. Hsu and Pipes [137] extracted the Al–8-hydroxyquinoline complex from 1000 mL of sample into 5 mL of benzene. A sensitivity increase of greater than 100-fold was achieved, but the large volume of sample required makes this approach impractical in soil solution studies.

Sensitivity of AAS for Al can be greatly improved through the use of graphite tube atomizers; detection limits of around 0.005 μM have been achieved using this method [138]. The sensitivity of the method is dependent on the nature and age of the graphite tube employed [139] and the nature of the sample matrix [140]. Several researchers have reported that AAS determination of Al using a graphite tube atomizer includes the majority of Al in particulate forms. Carrondo et al. [141] reported Al recoveries of 95–100% for type A zeolite, and Playle et al. [142] reported recoveries of 81–93% for kaolinite; particle size distribution in the sample was not reported in these studies.

A detection limit of $\approx 10\ \mu g\ L^{-1}$ can be achieved for Al by ICP-AES using the 396.15 and 308.21 nm lines [143]. Further improvements in sensitivity of ICP-AES for Al can be achieved using a sensitive line at 167 nm in the vacuum ultraviolet range [144]. Preconcentration using Chromazurol S immobilized on a silica gel achieved an enrichment factor of 50 [145]. As very high temperatures are produced in the plasma, it is anticipated that all forms of Al in the sample will be measured. Ambe and Nishikawa [146] found a recovery efficiency of >80% for Fe and Al in particles 0.4 to 1 μm in diameter. Lower recoveries were found for larger particles, which may be due to the behavior of these heavier particles during the aspiration phase rather than failure to atomize within the plasma.

4.4.2   Spectrophotometric Methods

Colorimetric methods for Al determination have been in use for many years and, despite the upsurge in popularity of spectroscopy, they are still widely used [136]. Colorimetric methods offer the advantages of low cost and equipment requirements, ease of use, and good sensitivity. A range of colorimetric reagents are available for the measurement of Al, although some are unsuitable for natural waters because of their low sensitivity or interference by commonly encountered ions [147]. Only the more sensitive and commonly used methods are considered here.

Aluminon was one of the earliest reagents used for the determination of trace amounts of Al [148]; however, the method offers only moderate sensitivity, as the absorptivity of the complex is $\approx 2 \times 10^4\ L\ mol^{-1}\ cm^{-1}$ [149], and most techniques require a heating step [150]. Jones and Thurman [151] developed a method for Al determination based on Eriochrome cyanine R (ECR). This reagent offers high sensitivity for Al with a molar absorptivity of $6.75 \times 10^4\ L\ mol^{-1}\ cm^{-1}$ [147]. Potential interferences from F, PO_4, and Fe may be a problem in natural waters.

Aluminum determination through the formation of the Al–8-hydroxyquinoline complex followed by solvent extraction of the complex and spectrophotometric measurement [152] is the most sensitive of the commonly used spectrophotometric methods [136]. Although the solvent extraction procedure adds an additional step to the method, the Al complex formed is stable in the organic phase; Bloom et al. [153] reported no change in absorbance after storage of the extract at ambient temperature for 24 hours. Polymeric Al and particulate Al have been reported to be excluded when extraction is performed at either pH 5.0 [153–155] or pH 8.3 [155]. Although this method offers good sensitivity and discrimination against particulate forms of Al, its applicability to soil solution studies is limited by the large volume of sample required (25 to 100 mL [153,155]).

Dougan and Wilson [149] compared the performance of aluminon, ECR, and a number of other reagents, including pyrocatechol violet (PCV), which had received little prior evaluation for Al determination. They found the PCV method

to be sensitive for Al, with a molar absorptivity of 6.3×10^4 L mol^{-1} cm^{-1}, and to be relatively free of interferences. Iron interference can be eliminated by reduction to the ferrous form and complexation with 1,10-phenanthroline. The simplicity of the PCV method of Dougan and Wilson [149] makes it well suited to automation [156]. Automation has been reported to offer increased precision, coefficients of variation being 6.8% for the manual method of Dougan and Wilson [149] and 2.9% for an automated approach [157]. A potential problem in automated methods is due to their speed of analysis. In automated methods, the sample is acidified to cause decomplexation of Al from organic ligands as a component part of the analysis; thus, the period of acidification prior to analysis is reduced to as little as 1 minute. As the kinetics of Al-fulvate interaction are relatively slow [158], it is unlikely that such a short period of acidification would result in effective decomplexation of Al from organic ligands. Rpgeberg and Henriksen [159] found little beneficial effect from addition of acid in an automated method and discarded acid addition in their final method.

Røyset and Sullivan [156] reported that natural organic ligands could compete with added complexing agents for Al, causing negative interference in the determination of Al. In a comparison of Al determination by PCV, ECR, and 8-hydroxyquinoline (pH 8.3) with extraction into methyl isobutyl ketone, Røyset and Sullivan [156] found that the 8-hydroxyquinoline method was not affected by the presence of humic and fulvic acids at 10 to 200 mg L^{-1} organic C. The presence of organic ligands did interfere with ECR at organic C concentrations greater than 50 mg L^{-1} and with PCV at organic C concentrations greater than 10 mg L^{-1}. However, this result is probably attributable to the short reaction time in the automated analytical method used. Dougan and Wilson [149] reported that the presence of humic and fulvic acids caused only a very small reduction in the Al concentration determined by PCV in acidified samples. Determination of Al without prior acidification resulted in underestimation by 5 to 10% and 30 to 50% in solutions containing organic C concentrations of 10 mg L^{-1} and 200 mg L^{-1}, respectively [156].

The interference caused by organic ligands in the determination of Al can be overcome by destruction of these ligands by photo-oxidation. The use of photo-oxidation of freshwater samples as a step in trace metal speciation schemes was pioneered by Florence [160], who reported that measurements of total Cd, Cu, Pb, and Zn before and after ultraviolet (UV) treatment showed no losses. In contrast, Laxen and Harrison [161] reported that irradiation of a number of river water samples resulted in a considerable increase in pH and loss of labile metals as measured by anodic stripping voltammetry. Campbell et al. [162] reported losses of $\approx$20% of the total Al content during photo-oxidation despite little change occurring in the solution pH during photo-oxidation. They attributed this loss to adsorption of Al by the quartz tubes used. Bloom and Erich [136] proposed that the Al losses

observed by Campbell et al. [162] were due to precipitation of $Al(OH)_3$ during heating of the samples; the solubility of $Al(OH)_3$ decreasing with increased temperature. Bloom and Erich [136] concluded that heating should be avoided during photo-oxidation or acid should be added to prevent precipitation.

Extremely sensitive determination of Al is possible using fluorimetric methods [147]. The most commonly employed reagent, lumogallion [3-(2,4 dihydroxyphenylazo)-2-hydroxy-5-chlorobenzene sulfonic acid], is reported to have a detection limit of 0.05 $\mu g\,L^{-1}$ [163], although this can be improved to 0.02 $\mu g\,L^{-1}$ by the addition of the nonionic detergent Triton® X-100 [164] or to 0.007 $\mu g\,L^{-1}$ by extraction into *n*-hexanol [165]. A method based on the formation of a 1:1 complex with chromotropic acid (1,8-dihydroxynaphthlene-3,6-disulfonic acid) in a methanol medium provides a linear response in the concentration range 2 to 100 $\mu g\,L^{-1}$, with a detection limit of 1.0 $\mu g\,L^{-1}$, and has been used successfully on tap, river, and seawater samples [166]. Fluorescence by dissolved organic matter and competition for Al by natural organic ligands may cause interference in fluorescence methods [163]. Further problems may arise through the high sensitivity of these methods accentuating the problems posed by Al contamination. Use of double distilled water is recommended, but storage should not be in glass [163]. Care should be taken to avoid containers that may contain fluorophoric compounds able to leach into solutions [136].

4.4.3 Speciation of Al

Aluminum may be present in solution in a variety of forms including Al^{3+}, inorganic ion pairs, organically complexed Al, and polymeric forms. Studies of the effects of Al on plant growth have indicated that these forms have different toxicities. Thus, it is often necessary to determine the speciation of Al in solution rather than the total concentration present. The activity of Al species in solution may be calculated from thermodynamic principles, and several computer speciation programs have been written to perform these calculations [167,168]. Although this approach has been successful in simple well-defined systems, it has proved less satisfactory in systems containing organic ligands. Hue et al. [125] used a computer-based mathematical model to calculate monomeric Al activity in the presence of short-chain carboxylic acids. Organic acid concentrations were determined by high-performance liquid chromatography, and the Al concentration was measured by ICP-AES. Poor agreement between calculated monomeric Al activity and root growth, relative to inorganic Al controls, was attributed to imprecise association constants and the failure of the analytical methodology to identify and measure all organic ligands. Thus, speciation of Al in natural waters by thermodynamic calculations, is, at present, precluded by analytical difficulties [125] and the lack of reliable association constants [69].

An alternative approach to the problem of speciation of Al in complex natural water systems has been the use of analytical methods that aim to measure spe-

cific forms of Al. These techniques include short-term reactions with complexing agents [153–155,169], dialysis [170,171], cation exchange resins [162,172], F^- ion-selective electrometry [80,172], ion chromatography [173,174], and the use of selective reagents [175,176]. This section briefly considers the applicability of a number of these approaches to soil solution studies, with particular emphasis placed on characteristics of the methods that restrict their use. A detailed review of Al speciation methods is given by Bloom and Erich [136].

The ion exchange column procedure [172] has been widely used for the speciation of Al in environmental samples [136]. Ion exchange attempts to separate inorganic and organically complexed Al by passing samples through an ion exchange resin that retains free hydrated metals and labile complexes. Inaccurate results may arise as a result of sample pH change occurring during passage of the sample through the exchange column and through disruption of the equilibria between the various Al forms [177]. Changes in pH can be minimized by matching column pH and cation composition to those of the sample [162]. Whereas preparation of columns compatible with sample composition may be appropriate in studies involving repeated samplings of river and lake waters, this approach is made impractical in soil solution studies by the diversity of solution compositions encountered. A more widely applicable approach presented by Powell [178] uses a solution–exchanger contact time of around 1 second to minimize disruption of sample equilibria.

Ion chromatography has received considerable interest as a means of separating Al forms [173,174,179]. The approach is capable of separating F-, oxalato-, and citrato-aluminum pairs [173,174]. However, phytotoxic Al^{3+} and nontoxic $Al-SO_4$ ion pairs were eluted together, the outer sphere $Al-SO_4$ complexes dissociating in the presence of the sulfonate exchange sites of the column resin [173]. The use of ion chromatography for the speciation of soil solutions may also be limited by the potential for redistribution of species due to differences in sample and eluent ionic strength and pH [173] and the adsorption of humic acids by the exchange resin [174].

Equilibrium dialysis has been used for the speciation of Al [170,171]; however, its use is restricted by the large volume of solution required and the length of time taken to reach equilibrium ($\approx$48 hours) [171]. Furthermore, the effectiveness of this approach may be limited by the potential for permeation of low-molecular-weight organic molecules through the membrane [170,180,181].

Several methods have been proposed that employ selective chelating agents to determine inorganic monomeric Al. Evans and Zelazny [175] proposed a method that utilizes the decrease in absorbance of crown ether at 273 nm due to chelation with Al^{3+}. Because no phase separation of the organic solvent containing the crown ether occurs in the proposed method, the humic and fulvic acids present in soil solution contribute a high background absorbance at 273 nm [177]. Morin has also been proposed as a reagent specific to inorganic monomeric Al

forms [176]; however, as Ca^{2+} and Mg^{2+} contribute interferences, this method is unlikely to prove effective in soil solution studies.

Short-term colorimetric methods are easy to use and require a small volume of sample. In general, these methods assume that only inorganic monomeric Al forms react with the chromogen during the reaction period used. Kerven et al. [177] demonstrated that, for five short-term colorimetric methods, this assumption was invalid. The best discrimination was achieved by a 15-second 8-hydroxyquinoline method [154]; this method measured 46% of organically complexed Al as inorganic monomeric forms. The remaining methods, which involved longer reaction times, measured >80% of the organically complexed Al as inorganic monomeric forms. The method of Kerven et al. [169] assumes that both inorganic and organic forms of Al will immediately begin to react with an added chromogen but that their rates of reaction will vary. This method uses a series of calibrating solutions containing a known total Al concentration prepared with varying ratios of inorganic monomeric Al and organically complexed Al. Aluminum in unknown samples is fractionated into inorganic monomeric and organically complexed forms on the basis of a short-term reaction with PCV or aluminon and a total Al measurement by ICP-AES.

5   CONCLUSIONS

In many acid soils, Al presents the primary challenge to plant growth; thus, the chemistry and phytotoxicity of Al have been extensively researched and are reasonably well understood. However, the identification of Al-toxic soils remains fraught with difficulties. Although it is generally accepted that measurement of the activity of phytotoxic ionic species in soil solution provides the best correlation with plant response, the cost and labor-intensive nature of this approach preclude its adoption for routine soil testing. Simpler measures, such as 0.01 M $CaCl_2$-extractable Al or measurement of soil pH, are inexpensive and sufficiently effective as predictors of Al toxicity to provide an effective routine soil-testing tool.

Identification of Mn-toxic soils is an even greater challenge than identifying those that are Al toxic. This difficulty stems from the ephemeral and heterogeneous nature of reducing conditions in soil and from the potential for interactions of Mn with several other plant nutrients. Further difficulties arise as typical soil-handling procedures, such as air drying, alter the soil Mn status. The most effective approach may be to use 0.01 M $CaCl_2$-extractable Mn and to consider the soil pH.

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11

Using Lime to Ameliorate Topsoil and Subsoil Acidity

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1 INTRODUCTION

This chapter considers the practice of liming—what information is required and hence what measurements should be made to answer the questions, is a soil acid, is lime required, and, if so, how much lime should be applied? These questions are approached from the practical perspective of an advisor in the field. Such questions go beyond the technical issues, and some discussion of the economic and indeed social and cultural issues related to liming is offered.

This chapter does not attempt to review comprehensively and condense the existing scientific literature. Rather, the approach is to attempt to put information consolidated in other reviews, including this book, into a practical context and framework.

The very concept of soil acidity and how it is measured has changed remarkably over the last 50 years as understanding has developed. The early concepts and definitions of optimal soil pH and lime requirement were based largely on what are now referred to as soils with permanent negative charge. It is now re-

alized, however, that most soils, especially acid soils, contain some variable negative charge. The "acidity" in such soils depends on the pH at which it is measured. This has, or at least should have, had a major effect on how soil acidity and lime requirements are measured and interpreted.

Such changes in response to new understanding are essential, but they can also give rise to confusion and, in the extreme, apparent conflicts in the scientific and advisory literature. This can be very difficult for "new" scientists, technicians, and advisors—those, it is suggested, at the "front line" in terms of making decisions about the need for lime. Furthermore, change required at the technical level can be resisted by cultural attitudes toward liming. These must also be challenged. For these reasons, the chapter begins by briefly tracing the origins and subsequent developments of some of the important concepts and measurements related to soil acidity, indicating where progress could be made to improve decisions about lime use.

For the purpose of this chapter, liming is defined as the application of ground calcium and/or magnesium carbonates, hydroxides, and oxides, although it is appreciated that the latter two types of products are seldom used in practical agriculture today.

2 SIGNIFICANT DEVELOPMENTS

2.1 Optimal pH

Historically, the "ideal" soil was thought to be one that contained no acidity. For some, this was initially taken to be pH 8.2 to 8.4 because this was the approximate pH of a soil in equilibrium with fine limestone. Others interpreted "no acidity" to mean that the cation exchange capacity (CEC) of the soil was 100% saturated with the basic cations (Ca, Mg, K, and Na). Because, by convention, CEC was measured at pH 7, this pH became the ideal [1,2]. No doubt this was reinforced by the simple chemical fact that at pH 7.0 the concentrations of acid (H^+) and base (OH^-) are equal.

With increasing field experience, it was soon realized that the optimal soil pH, i.e., the pH at which crop production was maximized, was not only different from the theoretical ideal but also different for different crops.

Russell [3] discussed the many problems in measuring and interpreting soil pH and concluded, "For general advisory purposes, there is no justification in measuring it to an accuracy of greater than 0.2 unit and probably to one greater than 0.5 unit." He outlined the conundrum as "Crops differ in their susceptibilities to these consequences of acidity; hence it is impossible to draw up any table showing the critical pH at which a given crop begins to suffer severely from acidity, even if any definite meaning could be given to the pH figure."

Russell also noted the discrepancy between laboratory- and field-determined lime requirements and the arbitrary choice of target pH inherent in defining lime

requirements, suggesting that "It [lime requirement] is a useful concept that can have no exact meaning." Consequently, he advised a pragmatic solution to the liming problem, suggesting that "The correct amount is found by continual check on pH or crop performance whenever additional dressings of lime are given."

Woodruff [4] was more precise. He stated, "the observation by Veitch (1902) that maximum crop yields were obtained by liming soils to less than pH 7 has been substantiated by numerous investigators." He suggested that this discrepancy arose because plants need only pockets of neutralized zones for maximum production.

In discussing the optimal pH requirements for a range of crops, Woodruff [4] went further, stating that "The actual soil pH requirements of crops are not in close agreement with the pH recommendations that are offered by the various advisory services." Reflecting perhaps a greater confidence in soil chemistry than agronomy, he stated, "Seldom are the results from field trials used to determine whether soils should be limed. Instead, chemical soil tests and other criteria are used to arrive at such decisions."

Despite all these reservations, most early texts provided readers with tables showing the degree of tolerance of various crops to acidity together with discussion of the laboratory methods for measuring how much lime is required to achieve pH 7 or greater.

This inconsistency can still be found today and arises from the early theories on soil acidity and practical experience in the field. The pH requirement has to a large extent been resolved at the technical level due to our better understanding of soil chemistry, particularly the chemistry of variable charge soils; agronomy; and plant physiology.

It is now more clearly understood that much of the acidity measured when soils with variable charge are titrated to a pH of 7 or 8.2 is pH dependent and does not affect the growth of the plant at the in situ soil pH [2,5]. For example, beginning with Kamprath [6] and Reeve and Summer [7], it is now accepted that on many soils it is primarily the Al component of exchangeable acidity that affects plant growth and that liming to reduce this component of acidity is sufficient to optimize plant growth. The optimal pH on such soils is consequently much lower than the "ideal" of 7 or 8.2. However, this applies only to soils in which Al toxicity is the major factor limiting growth (see Sec. 2.5).

The importance of the Al component of exchangeable acidity is reinforced by independent evidence from solution culture studies showing that most crops are not sensitive to H^+ ion toxicity per se but that small (μM) concentrations of Al can dramatically decrease plant growth (see Refs. 8 and 9 for examples). It is also beyond doubt that crop species, and cultivars within species, exhibit differential tolerance to Al (see Sec. 3.2 and Chapter 15).

With these developments, it is entirely appropriate to include in the definition of optimal pH the notion of "fitness for purpose." The ideal or optimal pH for

a given soil, in terms of crop production, must be defined in functional terms by including the crop and perhaps the cultivar to be grown.

2.2   Measuring Soil pH

Less progress has been made in modifying the techniques used to measure soil pH and trying to incorporate our recent understanding of acid variable charge soils.

It has been known for a long time that the soil pH—more correctly the pH of a solution in equilibrium with the soil—is affected by the strength of the electrolyte, among other things. Thus, temporal variations in soil pH were attributed to changes in soil moisture or recent additions of fertilizer [3]. The results in Fig. 1 are frequently used to demonstrate this relationship, often with the implication that soil pH is an unreliable measurement. It was for this reason that Schofield and Taylor [10] suggested that pH should be measured in 0.01 M CaCl$_2$ to eliminate these effects. This concentration was chosen because it was thought to represent the concentration of Ca in temperate soils. There is now clear evidence that the ionic strength (I) of soil solutions of field soils, including both temperate and tropical soils, is about 0.003 to 0.005 M [11–15].

There is also evidence that soil solution ionic strength varies in a predictable seasonal manner, being higher in the summer (low soil moisture) and lower in the
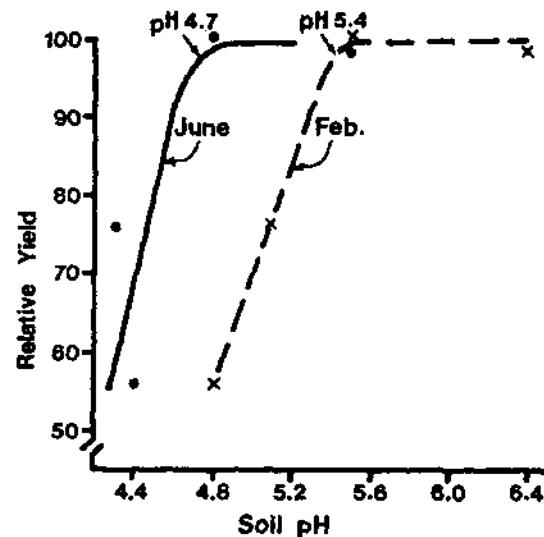
FIGURE 1   Effects of fertilizer application and sampling date on pH of an Ultisol; February sampling preceded fertilizer application to potato plants. From Ref. 5. Copyright 1994, American Society of Agronomy.

winter (high soil moisture). The pH of the soil solution and, to a lesser extent, the soil pH (if it is measured at a suitably low ionic strength) vary in a predictable inverse manner [12,13,16]. These effects can be large. For example, Edmeades et al. [12] measured seasonal extremes of 0.002 to 0.009 M in soil solution ionic strength and 6.0 to 6.5 in solution pH. The question arises, however, should the methods used for measuring soil pH, and indeed extractable Al and Mn, be modified to include these effects or eliminate them, as has been past practice?

It is reasonable to assume that plants respond to soil conditions through the medium of the soil solution. It is to be expected, therefore, that the pH and the concentrations and form of Al and Mn in the soil solution, at the prevailing field conditions, will have a significant impact on plant growth. There is some circumstantial evidence supporting this view, but further investigation is required.

Edmeades et al. [17] noted that pasture responses to lime are greatest in the summer–autumn seasons, corresponding to the time of highest ionic strengths and lowest pH. The implication is that Al toxicity is also expressed in a seasonal manner. They suggested, therefore, that it might be possible to improve the prediction of lime responses using methods that better reflected both the prevailing and constantly changing soil solution conditions.

More convincing, Carr et al. [18] accounted for 60% of the variation in wheat yields across a wide range of soils in Western Australia using subsoil Al, extracted at the soil solution concentration (0.005 M KCl). The ratio of Al to Na was superior to Al alone, suggesting that Na, an indirect measure of past fertilizer history, accounted for site-to-site differences. These results support [15] the suggestion of Slattery et al. that the form of Al extracted into solution at normal field ionic strengths might be quite different from the forms extracted into 0.01 M $CaCl_2$ ($I = 0.03$ M) and 1 M KCl ($I = 1$ M).

More studies, such as those by Dolling and Ritchie [19] and Edmeades et al. [20], are required to define the measurement conditions (soil/solution ratio, electrolyte type and strength) that best mimic the ionic strength prevailing in situ in the field. This work should be coupled with an examination of the concentration and speciation of Al and Mn.

2.3 Measuring Lime Requirements

There have been two reviews [2,21] of the many methods that have been developed to measure soil lime requirement—the amount of lime required to achieve a desired, and generally arbitrary, soil pH.

The basis for most of these methods, and in particular the choice of the desired pH, can be traced back to the early concepts of soil acidity—exchangeable acidity or base saturation [2,5]. As discussed earlier, these concepts are no longer appropriate, especially on variable charge soils. Other methods for measuring lime requirements that use or are calibrated against a laboratory-determined lime

requirement are equally flawed, given the discrepancy that exists between field- and laboratory-determined lime requirements [3,5].

For these and other reasons, both reviewers [2,21] expressed caution about the use of these methods. In particular, Black [2] made an important distinction between the soil lime requirement, the amount of lime to achieve an arbitrary desired pH, and the biological lime requirement (BLR), the lime required to eliminate restrictions to plant growth.

The best early example of this move toward defining the soil lime requirement in terms of the biological lime requirement for the plant comes from the work of Kamprath [6] and Reeve and Sumner [7], but others have also embraced the concept. In New Zealand, Edmeades et al. [22], having shown that the biological optimal pH for pasture is 5.8 to 6.0, used data from field trials to determine the amount of lime required to achieve pH 6.0—the field lime requirement, or to use Black's concept, the biological lime requirement. Slattery and Coventry [23] adopted a similar approach in Australia for a range of crops and soils, defining the lime requirement as the amount of lime to obtain 90% of maximum yield.

Interestingly, the preceding studies suggest that it may be possible to determine the BLR from simple soil measurements that are routinely made. For a set of New Zealand soils, the field lime requirement was correlated with the initial soil pH and the organic matter content [24]. Bailey et al. [25] found similar results in the United Kingdom (UK). For some Australian soils [23], the initial soil pH, together with soil Al, was a useful predictor of field lime requirement.

Although these approaches are useful and accommodate our modern understanding of the soil–plant acidity complex, what is urgently required is field information defining the buffer capacity of soils—the unit change in soil pH per unit of acid or base applied. Such information, together with the initial pH and the optimal pH, could be used to determine the biological lime requirement for any given crop $\times$ soil combination (see Sect. 3.3.1). Furthermore, such information is essential for predicting the magnitude of soil pH changes that result from management-induced soil acidification.

2.4 The Acidification Process

It is now understood that soil acidification is not solely the result of the properties of the parent material and weathering but also occurs as a result of management practices. The major processes contributing to soil acidification under agricultural systems are now well understood as detailed by Helyar and Porter [26] and De Klein et al. [27] or more simply by Hollier [28].

The question of whether lime is required is no longer restricted to soils that are currently acid. Lime is also required on soils that are currently at their biological optimal pH to prevent them from become more acid. The thinking, and hence research, must go beyond the question of how much lime is required to achieve

the optimal pH and include the assessment of how much lime is required to maintain the optimal pH.

Several models of the soil acidification process in cropping and pastoral systems have been developed [26,27]. These are very useful tools, and it is now possible to calculate the amount of acidity or alkalinity produced by any pastoral or cropping system. Some typical estimates are given in Table 1. However, the technical limitation confronting the practical application of these acidification models is information on the buffer capacity of soils in the field required for converting the rates of acid produced into the amount of lime required to neutralize this acidity. The publications by Ridley and Coventry [32] and De Klein et al. [27] highlight this problem. Unfortunately, there is a paucity of data on this topic (Table 2). Why this should be so, when it is such a fundamentally important measurement in terms of making lime decisions, is difficult to understand, especially given the low cost involved in making such measurements.

What is remarkable is that the amounts of lime required to neutralize the acidity produced in cropping and pastoral systems, and hence maintain the soil pH, are not large on an annual basis, ranging from about 100 to 600 kg ha^{-1} of limestone. From an economic perspective, problems arise because of the compounding nature of soil acidification over a long period of time, the remedy for which is large capital inputs of lime at rates of several tonnes per hectare. This frequently puts the cost of remedial action beyond the reach of the individual farmer. In this respect, the solution to the soil acidity problem facing many countries is similar to that of correcting P deficiency. The farmers may be able to pay for the ongoing maintenance inputs of P once the soil is productive, but the initial capital input to achieve this is beyond their resources.

An important consequence of the better understanding of the soil acidification process is that there is now a greater awareness of subsoil acidification as a factor limiting soil productivity. Even if the topsoil is sufficiently fertile, plant growth may be limited by subsoil acidity affecting its access to water and reducing its tolerance to drought [39,40]. Decisions about the need for lime must go beyond the "plow layer" and must take into account the subsoil.

2.5 Understanding the Specific Effects of Acidity on Plant Growth

Much progress has also been made unraveling the specific causes of poor plant growth in acid soils. This has provided further independent evidence that the old concept of the ideal pH soil is no longer tenable.

There is currently much emphasis on Al and Mn toxicity as factors limiting plant growth on acid soils. But this needs to be put into context. Although Al and Mn toxicity may be problems on many acid soils, nutrient deficiencies such as Ca, P, N, and Mo are also widespread. As increasing the soil pH by liming can in-

TABLE 1 Summary of Reported Rates of Acidification

Country	System	Acidification rate (kg lime ha^{-1} year^{-1})	Comments	Reference
New Zealand	White clover–based pasture	75 to 90	Model calculation Based on pH change	De Klein et al. [27]
New Zealand	White clover–based pasture	150 to 170 300 to 600	Based on amount of lime to maintain soil pH	Edmeades et al. [29]
Australia Vic	Subterranean clover–based pasture	10 (no fertilizer) 70 (fertilizer) 140 (fertilizer + lime)	Based on pH change	Ridley et al. [30]
Australia Vic	Subterranean clover–based pasture	100	Estimated from measurement of nitrate	Ridley [31]
Australia Vic	Perennial pasture	150	leaching and calculation of product removal	
Australia Vic	Legume-based pasture	125 to 300	Based on pH change	Ridley and Coventry [32]
Australia NSW	Legume-based pasture Cereal–legume rotations	5 to 180 50 to 370	Based on pH change	Helyar et al. [33]
Australia Vic	Wheat Lupins	230 625	Based on pH change	Slattery et al. [34]
United Kingdom	Not specified Legume-based pasture Grass + N fertilizer	195 300 to 600 1400 to 1700	Based on acid deposition Model calculation	Johnston et al. [35] Kennedy [36]

TABLE 2 Estimates of Soil Buffer Capacities Based on Field Data

Country	Soils	Field buffer capacity, lime (tonnes) ha^{-1} (pH unit)$^{-1}$	Reference
New Zealand	Range of 36 from throughout NZ	5 to 15 (0 to 7.5 cm)	De Klein (personal communication) based on data from Edmeades et al. [24]
Australia	Range of 11 soils in NSW	1.1 to 2.6 (10 cm)	Hochman et al. [37]
United Kingdom	Sands and loamy sands	6 (0 to 20 cm)	Goulding and Annis [38]
	Sandy loams and silt loams	7 (0 to 20 cm)	
	Clay loams and clays	8 (0 to 20 cm)	
	Organic (100 to 250 g OM kg^{-1})	10 (0 to 20 cm)	
	Peats (>250 g OM kg^{-1})	16 (0 to 20 cm)	

OM, organic matter.

crease the availability of these nutrients, a plant response to liming cannot be assumed to be due solely to the alleviation of toxicity. Conversely, the full extent of acid soil toxicity cannot be determined until these other confounding effects are eliminated or accounted for.

While acknowledging that liming an acid soil can have many effects, including physical and biological (see Ref. 41 for a recent review), the most important nutritional problems on acid soils, at least over the range of soil pH normally encountered, are listed in Table 3.

Identifying which of these factors, either singly or in combination, are operating on a given soil can have a large impact on the amount of lime required for remedial action, as these mechanisms operate over different ranges in the soil pH continuum. For example, it is now known that many acid soils in New Zealand and Australia were Mo deficient, and large responses to liming in legume-based pastures were observed. When Mo deficiency was specifically diagnosed and its interaction with soil pH resolved, farmers could obtain similar yields with small inexpensive applications of Mo rather than large dressings of lime (see review in Ref. 17). The economic advantages, at least in the short term were obvious. Similarly, on soils where the primary factor limiting plant growth is Al toxicity, rela-

TABLE 3 Important Limitations to Plant Growth on Acid Soils

Factor limiting plant growth	Effect of liming	Typical conditions of occurrence
Al and Mn toxicity	Increases soil pH and reduces amount of phytotoxic A1 and Mn	pH <5.5, acid parent material
Ca deficiency	Supplies Ca	Highly weathered soils with low effective cation exchange capacity (ECEC)
Mo deficiency	Increases pH and increases Mo availability	Many soils derived from sedimentary, granitic, and metamorphic parent material
N deficiency	Increases pH and enhances net mineralization of organic N	Moderate acidity (pH 5.5 to 6.2), high soil organic matter, temperate soils
P deficiency	Decreases P sorption, increases solubility of P/Al and Fe minerals, increases mineralization of organic P	Soils with pH <5.0 and high content of active Al and Fe to which fertilizer P applied. Otherwise rare
Induced deficiency (Zn and Mn)	Increases pH and decreases the availability of Zn and Mn	High soil pH (>6.5), soils with low field buffer capacity (e.g., sands and soils with low organic matter)

tively small inputs of lime to bring the soil pH up to about 5.5 are all that is required for near-maximum production [6,7].

The same logic must apply to Ca. Applying small amounts of Ca to remedy Ca deficiency will cost less, it is assumed, than applying lime to change the soil pH. There is evidence indicating that Ca deficiency may be more prevalent than previously acknowledged on tropical acid soils [39,42,43].

Most acid soils are also extremely P deficient, a problem usually exacerbated by the presence of active Fe and Al oxides. Large amounts of P fertilizer are required in addition to liming to make them productive. Although there is a large amount of literature on the effects of soil pH on soil P availability, much of it is conflicting and confusing. Two reviews [44,45] concluded that, despite common myth, liming does not frequently have beneficial effects on soil P availability, as distinct from its effect on changing the ability of the plant to reach already avail-

able P, by reducing Al or Mn toxicity or deficiency of N and Mo. Edmeades et al. [45] referred to these processes as type A or type B, respectively, and noted that it is frequently the type A processes that are inferred in the generalization that liming increases P availability but it is often data related to type B processes that are used as evidence.

These two types of processes are frequently confused [17,45], but their distinction is important. It is only when the type A processes are operating that liming can be used as a means of reducing fertilizer P inputs. On the other hand, where type B processes are operating, the efficiency with which applied fertilizer P is used can be greatly increased.

There is now a greater understanding of the dangers of overliming, particularly in relation to increasing the risk of Zn and Mn deficiency. Overliming in this respect does not necessarily mean liming to soil pH levels above 7.0, for these effects can and do occur on some soils at lower pH levels [27].

3 COMPONENTS OF THE DECISION PROCESS

Given the preceding discussion, it should be clear that decisions regarding the need for lime are not simple. There are now many questions and options to consider (Fig. 2). These are grouped in four components in Fig. 2. The first three components—the soil, the plant, and the system—deal with the biophysical aspects that need to be considered. The factors affecting the economics of liming make up the fourth component. But all of these decisions must be made within the context of the prevailing social and cultural attitudes. What might otherwise seem an obvious decision at the biophysical level can frequently be confused at the social and cultural levels.

3.1 The Soil

3.1.1 Soil pH × Depth Profile

The first question at the biophysical level, although not necessarily at the cultural level, is whether the acidity-induced factors limiting plant growth are present in the topsoil, subsoil, or both. This will determine whether lime should be surface applied or incorporated in the topsoil or subsoil.

Thus, the first step is to measure the soil pH and extractable Ca, Al, and Mn at various depths in the profile. In the first instance, it is suggested that the sampling depths should reflect the pedological horizons, but it is noted that soil acidification can be stratified over a small scale (20 to 40 mm) within the soil horizon [46]. It is also desirable to use methods that reflect the prevailing ionic strength of the soil solution [18–20].

Sumner [40] provided examples of the pH and Al profiles of eight soils and distinguished between two groups, depending on the acidity of the parent material
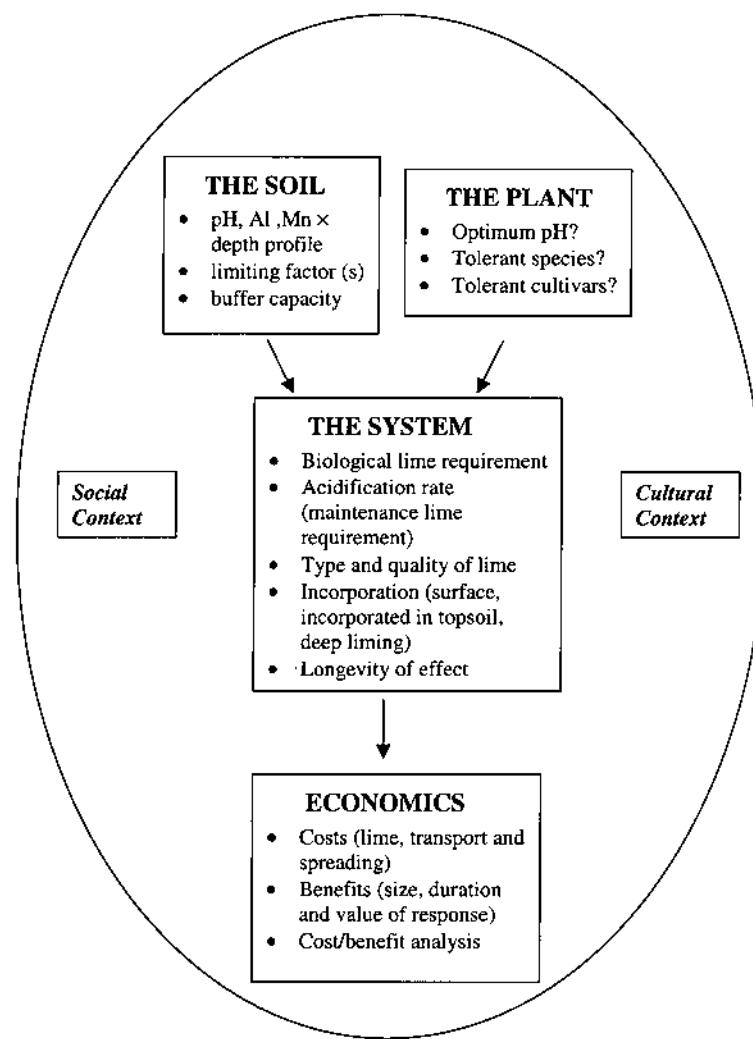
FIGURE 2 A process for deciding on the biophysical need for lime.

and the subsequent acidification due to management practices. Soils in the first group, referred to here as group 1, are typically from tropical and humid subtropical regions. They have naturally acid topsoils and subsoils, some of which have become more acid through management practices. They generally have a large component of variable charge, and their pH and effective CEC decrease with increasing soil depth. These soils are likely to exhibit both Al toxicity and Ca deficiency.

The second group (group 2) comprises soils from subhumid, subtropical, and tropical regions and humid temperate regions. They do not normally have subsoils acid enough to limit root growth but may have developed acid topsoils due to acidifying management practices. They have less variable charge, a higher effective CEC, and are unlikely to be Ca deficient. For these soils, pH increases with increasing depth.

Helyar [47] emphasized the same soil-forming factors, parent material, weathering, and subsequent management in describing the types of soil pH profiles typically found in New South Wales (NSW), Australia (Fig. 3). There are
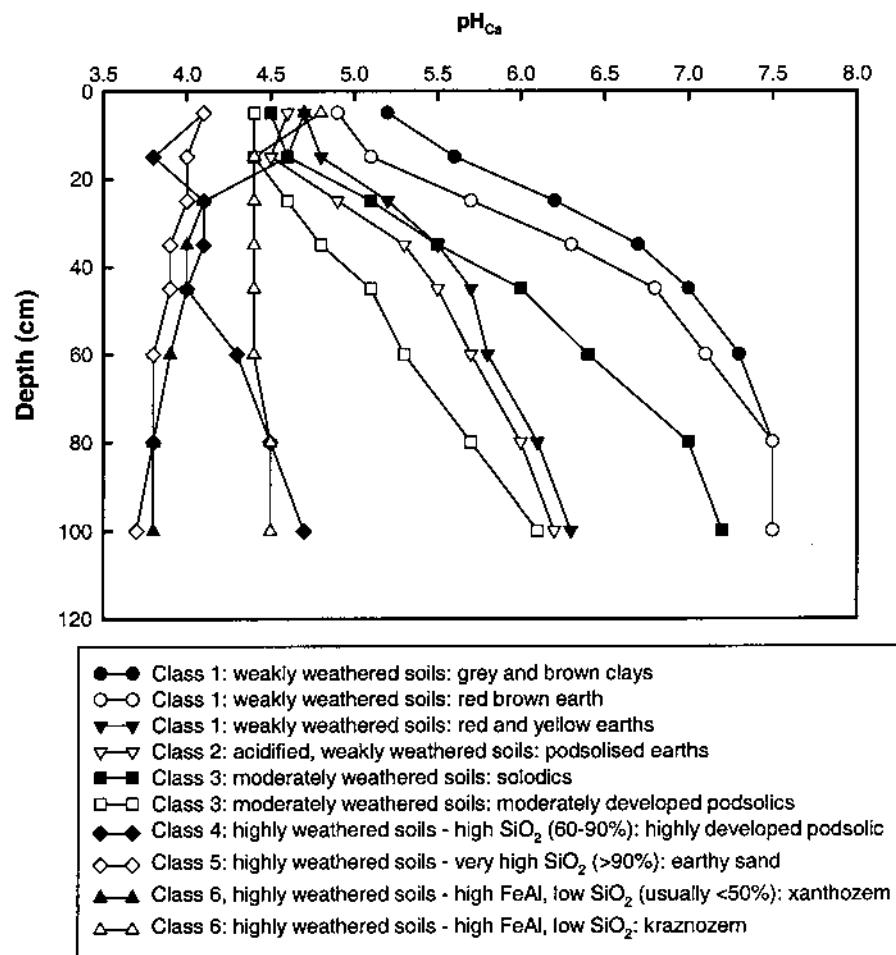
FIGURE 3 Soil pH profiles typical of the soil types in NSW, Australia. (From Ref. 47.)

other examples of soil pH profiles in the literature (Adams [5], 4 soils in southern United States: Scott et al. [46], 15 sites in southeastern Australia: Moody and Aitken [48], 4 sites in Queensland, Australia: Wheeler [49], 12 sites in the North Island, New Zealand; Farina et al. [50], 1 site, South Africa).

Soil pH profiles can change significantly over time due to management practices. Moody and Aitken [48] measured the long-term consequences of three management systems for soil pH profiles in Queensland. Similarly, Adams [5] gave examples of the short-term effects (5 years) of Bermuda grass, fertilized with N. These are all group 1 soils, using Sumner's [40] definition, and in all cases there was net acidification.

Other studies have examined the long-term effects of management practices on group 2 soils. For example, Ridley et al. [30] examined the effects of 73 years of legume-based pasture on the soil pH profile. In the absence of lime, this system had a net acidifying effect. Wheeler and Addison [51] resampled 35 reference sites in New Zealand, 30 years after they were first sampled and analyzed. Fifteen of the original sites remained under legume-based pasture and were subject to the normal agricultural practices, including possibly liming. For 7 of the 15 sites, there was net acidification equivalent to a decrease in pH of 0.43 units. The pH of the other 8 sites increased by 0.40 units. There can be no doubt that the processes that contribute to soil acidification, including product removal, organic matter accumulation, and nitrate leaching, are occurring to varying extents on these soils. It is reasonably assumed, therefore, that the absence of acidification on half of these sites is due to topsoil liming, as widely practiced in New Zealand legume-based pastures.

Comparing new soil pH profiles with these examples could provide useful insights into future management and appropriate liming strategies.

3.1.2   Determining the Primary Growth Limiting Factor

Any decision about lime application must also take into account the nature of the acidity—what is the primary factor limiting plant growth? As previously discussed, the answer to this question can have a profound effect on the amount of lime required to maximize production. However, it is difficult to make an unambiguous diagnosis because all liming experiments are confounded. It is impossible to alter one soil acidity constraint without simultaneously altering others. Because of this, liming experiments need to be carefully designed to eliminate all the possible confounding effects and hence deduce the mostly likely limiting factor. Applications of trace elements and fertilizer N should eliminate the possibility that these nutrients are confounding factors. Measuring the response to lime in the presence and absence of applied P and Ca (as a neutral salt) and examining their interactions can assist in separating the effects of liming on Ca deficiency and soil P availability from those due to Al toxicity per se. Plant analysis can also be useful, especially for diagnosing Mn toxicity and Mo and Ca deficiency. For a more thorough discussion, see Edmeades et al. [17] and for examples of the approach

required see Adams and Moore [42], Bruce et al. [43], Edmeades et al. [45], Black [2], and Wheeler et al. [52].

3.1.3 Soil Buffer Capacity

The field buffer capacity is essential for prescribing the amount of lime required to achieve the optimal pH (see Sec. 3.3.1). It is also required to predict the effect of ongoing acidification on soil pH.

Based on data from 36 field trials [24] on temperate soils in New Zealand, De Klein (personal communication) has calculated field buffer capacities of between 100 and 300 (average 170) kmole ha^{-1} (pH unit)$^{-1}$ [5 to 10 tonnes ha^{-1} (pH unit)$^{-1}$] (Table 2). They were not related to the soil properties CEC, total exchangeable bases, organic matter, soil texture, and extractable Al.

In the UK, "lime factors" have been derived empirically and are related to soil texture and topsoil depth. Figures range from 4.5 tonnes ha^{-1} (pH unit)$^{-1}$ on sandy grassland soils (0 to 15 cm depth) to 16 for arable organic soils (0 to 20 cm depth) [38].

Hochman et al. [37] used the term lime responsiveness index to describe the change in topsoil (10 cm) pH 1 year after lime application in 13 field experiments in NSW Australia. Figures ranged from 1.1 to 2.5 tonnes ha^{-1} (pH unit)$^{-1}$. Because of the short duration of the trials, these are likely to overestimate the real buffer capacity, but what is interesting is that they could be predicted based on the initial pH, total exchangeable cations, organic matter, and extractable Al. More work of this type is desirable to determine whether soil field buffer capacities can be readily predicted from simple soil measurements.

Although it would be desirable to develop a laboratory test to estimate the field buffer capacity, the history of lime research indicates the futility of this approach [3,5,24,32,40,53]. In any case, the buffer capacity of a soil in situ can be determined readily at little expense. The only requirements are a field trial with several rates of lime, a pH meter, and annual sampling and measurement of soil pH over a long period of time (3 to 5 years).

3.2 The Plant

3.2.1 Size of Lime Responses

The striking features of the international data on plant responses to liming are the wide range of reported responses for a given crop and the size of the largest responses (Table 4). The exceptions appear to be the pasture responses to liming on mineral soils in New Zealand.

Such data are difficult to interpret and are therefore of limited value. Most reviewers, while noting these very positive effects, emphasize the unpredictable nature of the responses. The difficulty, as Sumner [21] noted, is that the conditions under which most of these field trials were conducted have not been recorded in

TABLE 4 Range and Typical Responses of Crops and Pastures to Surface Application of Topsoil Incorporated Lime

Country	Crop	Soil acidity	Absolute range and typical range[a] of response to lime (% relative to control)	Reference
New Zealand	White clover–based pasture (mineral soils)	pH_W 5.0 to 6.0	0 to 10 (about 5)	Edmeades et al. [22]
	Clover-based pasture Organic soils	PH_W 4.0 to 5.0	10 to 140 (50 to 100)	
Australia NSW, Vic	Subterranean clover–based pasture	pH_{Ca} 4.2 to 4.7	−15 to 170 (20 to 60)	Scott et al. [46]
	Phalaris pastures	pH_{Ca} 4.1 to 5.0	0 to 900 (30 to 100)	
	Cocksfoot pastures	pH_{Ca} 4.1 to 5.0	0 to 70 (about 20)	
Australia NSW, Vic	Wheat	pH_W 5.0 to 6.0	0 to 38	Coventry et al. [54]
United States, southern	Cotton	pH_W 5.0 to 5.4	0 to 400 (10 to 30)	Adams [5], Adams and Pearson [55]
	Corn	pH_W 4.7 to 5.5	11 to 56 (10 to 30)	
	Soybean	pH_W 4.7 to 5.8	0 to 56 (30 to 50)	
	Alfalfa	pH_W 4.7 to 5.8	150 to >1000 (100 to 200)	
	Other forage crops[b]	pH_W 4.3 to 5.5	0 to 250 (10 to 30)	
United States, midwest	Corn	pH_W 5.0	75 to 96[c]	McLean and Brown [56]
	Soybean	pH_W 5.0	70 to 91[c]	
	Alfalfa	pH_W 5.0	20 to 84[c]	
Various[d]	Soybean	A1 base saturation 75%[f]	25 to 95[g]	Dierolf et al. [57]
	Corn	A1 base saturation 75%[f]	66 to 95[g]	
	Various[e]	A1 base saturation 75%[f]	80 to 95[g]	

[a] Typical value by visual inspection of the data.
[b] White clover, crimson clover, bermudagrass, millet, sorgham, ryegrass.
[c] Response at pH 5.0 relative to maximum yield.
[d] All tropical soils (Oxisols and Ultisols) from 10 countries.
[e] Groundnut, rice, cowpea, mungbean, pigeon pea, cassava, tanier, yams, sugarcane.
[f] A1 base saturation % of ECEC.
[g] Response at A1 saturation of 75%, relative to maximum yield

sufficient detail in the literature. It is therefore impossible to relate the size of the observed responses to any meaningful soil parameters or explain the lack of lime responses in some circumstances.

Various reasons have been advanced to explain the lack of ability to predict lime responses to plants [5,17,21,46]. The most important of these are (1) procedural differences in the methods of measuring the relevant soil properties, (2) procedural differences in the methods used to measure plant responses to liming, (3) seasonal and year-to-year differences in responses to lime, (4) genetic differences within species in their tolerance to acidity, (5) differences between soils in the nature and intensity of the acidity not accounted for in simple soils tests such as pH and extractable Al, (6) the confounded nature of the effects of liming on soil processes and the failure to control or eliminate these through trial design, and (7) the presence or otherwise of subsoil acidity.

This inability to predict reliably crop responses to liming seriously limits the use of lime as a solution to the soil acidity problem, as scientists are understandably reluctant to be positive about the benefits of liming without having a sound technical basis. However, as noted by Edmeades et al. [17], there has been progress in developing predictive relationships between plant yields and simple diagnostic criteria (for examples see Refs. 18, 22, and 57–60]. More work of this nature is urgently required to provide a sound biological basis for predicting crop responses to liming (see also Sec. 11.3.4).

3.2.2 Tolerance of Species and Cultivars to Soil Acidity

It has been known for a long time that plant species differ in their tolerance to soil acidity [61]. Most early textbooks (e.g., Russell [3]) provided tables of the relative tolerance of different species to soil acidity. However, a species that is tolerant to acidity at one site may not necessarily thrive on another acid soil. The specific cause of the acid infertility, and the plant's adaptation to it, needs to be identified and linked before such information can be used generally [62]. Also, large genotypic variability within species can result in overlapping in acid tolerance between species. Thus, such lists (Table 5) must be treated cautiously.

Much research has been directed to exploiting this variability to develop acid-tolerant species and cultivars, and today it is possible to be more specific and rank species according to their tolerance to one specific acid soil constraint, such as Al toxicity (Table 5) or Mn toxicity (see Chapter 10). With information such as this, it is now possible to choose species and cultivars that are better adapted to the prevailing soil conditions. This has become the basis for developing low-cost options for maintaining and increasing plant production on acid soils. However, this approach is limited by the range of tolerance that can be introduced into the important food plants.

Furthermore, using acid-tolerant species does not mean that lime will no longer be required. Soils will continue to acidify even when tolerant species are

TABLE 5 Aluminum Tolerance of Some Crops and Pasture Plants

Aluminum tolerance category	Plant species/cultivar
Highly sensitive	Alfalfa
	Most annual medics
Sensitive	Canola
	Some wheats
	Most barley
	Buffel grasses
	Most phalaris genotypes
	Lespedeza*
	Cotton*
	Sorghum*
	Soybean*
	Tobacco*
Tolerant	Rye grasses
	Tall fescue
	White clover
	Some cocksfoots (orchard grass)
	Some wheats
	Subterranean clover
	Albus lupins
	Dallisgrass*
	Corn*
	Rice*
	Peanuts* (except to low Ca)
Highly tolerant	Some cocksfoots (orchard grass)
	Pioneer rhodes grass
	Some lovegrasses
	Paspalum
	Kikuyu
	Maku lotus
	Narrow-leaf lupins
	Slender serradella
	Most oats
	Most triticale
	Yellow serradella
	Cereal rye*
	Bermuda grass*
	Bahia grass*

Source: Ref. 46 or Ref. 5 for those marked*.

used. This will mean that either increasing tolerance will need to be bred into the important cropping species or, at some point, liming will need to be introduced into the management system. For these reasons more, not less, emphasis should be given to liming soils as the long-term solution to acid soil infertility.

3.2.3 Acid Tolerance and Drought Tolerance

There is an important interaction between plant tolerance to soil acidity, in particular Al toxicity, and tolerance to moisture stress. This interaction can cause confusion and can be a confounding factor in plant responses to liming in the field.

It has long been known that Al toxicity inhibits root growth [63]; there are many examples of this phenomenon in the literature. Thus, a plant exposed to Al toxicity also exhibits intolerance to moisture stress because the root system is unable to exploit fully soil moisture reserves [5,39,40].

Perennial plants can adapt to moisture stress by adjusting their perenniality. For example, annuals can escape moisture stress by "dying" over the summer period. If such a plant is grown on an acid soil and at the same time is exposed to moisture stress, it may appear as if it is tolerant to acidity when in fact its survival is not related to an adaptation to acidity.

The problem becomes even more complex when naturally deep-rooted plants, which may or may not be acid tolerant, are grown on soils with either acid topsoils or subsoils. The effects of these various combinations on the likely response to liming are explored conceptually in Table 6. For example, a sensitive species (such as lucerne or canola) is likely to be very responsive to liming if topsoil acidity is the only limitation. Conversely, the expected response would be small for acid-tolerant crops such as cereal rye or oats. If a soil had strongly acid subsoil, then a sensitive and deep-rooted species such as lucerne would not respond well to topsoil amelioration. This interaction between acid tolerance, drought tolerance, and rooting depth could be a major source of variation in plant responses to lime, as discussed in Sec. 3.2.4.

3.3 The Agricultural System

3.3.1 The Biological Lime Requirement

Using Black's [2] definition, the biological lime requirement (BLR) can be defined for a given soil and crop as

$$\text{BLR (tonnes ha}^{-1}) = (\text{optimal pH} - \text{current pH}) \times \text{BC [tonnes (pH unit}^{-1})]}$$

where the optimal pH is the soil pH required for the specific crop or cropping system, the current pH is the pH of the topsoil, and the buffer capacity (BC) is the amount of lime (tonnes) to increase the pH of the topsoil by 1 unit. This is only

TABLE 6 Effect of Plant Type (Acid Sensitive or Moderately Tolerant) with Soil Acidity (Acid Topsoil or Acid Topsoil and Subsoil) and Rooting Depth (Shallow or Deep) on Likely Response to Liming

Soil type	Plant tolerance to acidity	Rooting depth[a]	Likely lime response[b]
Acid topsoil only	Acid sensitive	Shallow	Large response
		Deep	Large response
	Moderately tolerant	Shallow	Nil or small response
		Deep	Nil or small response
Acid topsoil and subsoil	Acid sensitive	Shallow	Response dependent upon depth of root extension into subsoil without acid soil limitation
		Deep	No response, poor growth
	Moderately tolerant	Shallow	Small response
		Deep	Moderate response if liming of topsoil markedly increased root proliferation and thus nutrient access

[a] Shallow rooting depth—it is assumed that roots are largely confined to the topsoil, whereas deep rooted is assumed to mean that roots extend well into the subsoil.
[b] It is assumed that sufficient lime has been applied to overcome the soil acidity limitation of most or all of the topsoil.

the amount of lime required to achieve the optimal pH and does not consider how much lime is required to maintain the optimal pH. The maintenance lime requirement (MLR) can be defined as

$$\text{MLR (kg ha}^{-1}\text{ year}^{-1}) = \text{acidification rate (kmoles H}^+\text{ ha}^{-1}\text{ year}^{-1}) \times 50$$

The acidification rate can either be determined using one of a number of models [26,27] or estimated from published data. A summary of available data was given in Table 1.

The quality of the lime can readily be factored into these calculations provided its lime equivalence is known. The hardness and the particle size of the lime also need to be considered, but these factors are more relevant to how quickly and how long the effects of liming will last. They will be dealt with latter (Secs. 3.3.2. and 3.3.3.).

3.3.2 Placement of Lime

The placement of lime is important because it affects how quickly, to what depth, and over what period of time the effects of lime are required. The option chosen—surface application, topsoil incorporation, and/or subsoil amelioration—will depend on the answers to these questions.

Two reviews [40,46] have discussed the various mechanisms—chemical, biological, and physical—by which surface-applied and surface-incorporated lime could affect soil acidity below the level of incorporation. Both concluded, however, that the accumulated results were too variable to reach a definitive conclusion in terms of how far the effects of liming penetrated down the profile. This view needs challenging.

Lime is a relatively insoluble material and the products of liming, alkalinity in the form of OH^-, HCO_3^-, and CO_3^{2-}, move through the soil slowly, taking many years. This is readily accepted for the reverse process, anthropogenic acidification, but nevertheless data from short-term trials are frequently used to test the hypothesis that lime does or does not move into the soil beyond the depth of placement [40,46].

The data from Sumner [40] and Scott et al. [46] are reassessed in Table 7, using only the data from trials that went for >10 years and adding other examples from the literature. In all cases, liming affected the soil below the level of placement. These results should not be taken to imply that it takes at least 10 years for surface liming to affect the subsoil. The data in Table 7 have simply been selected to demonstrate that the effects of liming below the level of incorporation occur slowly and that it is inappropriate to reject the hypothesis on the basis of short-term trials.

Other examples from the literature demonstrate quicker effects. In New Zealand, Doak [70] found that liming at 2 tonnes ha^{-1} (rainfall 800 mm) increased the pH at 15 to 25 cm, 2 years following liming, and that the maximum effect at this depth occurred 4 years after surface application (Fig. 4). Wheeler [64] reported similar results under almost identical circumstances. The maximum effect of surface-applied lime on soil pH occurred 2, 5, 12, and 15 years for the depths 0 to 50, 50 to 100, 100 to 150, and 150 to 200 mm, respectively, following surface application of 7.5 tonnes lime ha^{-1}. At higher rainfall (1500 mm year^{-1}) the effects are even quicker (Fig. 5) [49].

Similarly, in Australia, Ridley and Coventry [32] reported increased pH in the 100 to 2000 mm depth 5 years after surface incorporation (100 mm) of 5 tonnes ha^{-1} (rainfall 800 mm year^{-1}). Conyers and Scott [71] found substantial increases in pH below the depth of incorporation 5 years after application of 8 tonnes lime ha^{-1}. Two tonnes ha^{-1} had no effect below the depth of incorporation.

It is concluded, therefore, that surface liming, and the incorporation of lime into the topsoil, can and does reduce soil acidity below the depth of incorporation,

TABLE 7 Summary of Long-Term Trials Showing the Effects of Liming Below the Depth of Incorporation

Location	Soil	Lime rate (t ha^{-1})	Lime placement	Duration (years)	Depth of effect (cm)	Reference
New Zealand	Pallic	7.5	Surface	15	20	Wheeler [64]
Australia NSW	Granite	3.6	Surface	10	20	Cumming [65]
Australia NSW	Basalt	5.0	Surface	10	20	
Australia NSW	Red earth	5.5	Surface	13	20	Horsnell [66]
Australia NSW	Red earth	3.3	Surface	13	15–30	
Australia NSW	Yellow duplex	3.6	Incorp. 10 cm	12	20–30	Broemfield et al. [67]
Australia NSW	Yellow duplex	5.6	Incorp. 10 cm	12	30	
Australia NSW	Red earth	3.3	Incorp. 5 cm	13	10	
Australia NSW	Red earth	5.5	Incorp. 5 cm	13	20	
Australia Vic	Yellow podzolic	11.25	Surface	40	50	Ridley et al. [30]
South Africa	Plinthic paleudult	25	Incorp. topsoil	11	?	Farina et al. [50]
United States, Connecticut	Typic dystrochrept	16	Incorp. topsoil	20	50	Brown et al. [68]
United States, Connecticut	Typic dystrochrept	10	Incorp. topsoil	18	90	Brown and Munsell [69]
United States, Alabama	Not given	0.5 and 0.8 annually	Incorp. topsoil	32	45–60	Adams [5]
United States, Alabama	Not given	0.5 and 0.8 annually	Incorp. topsoil	32	45–60	
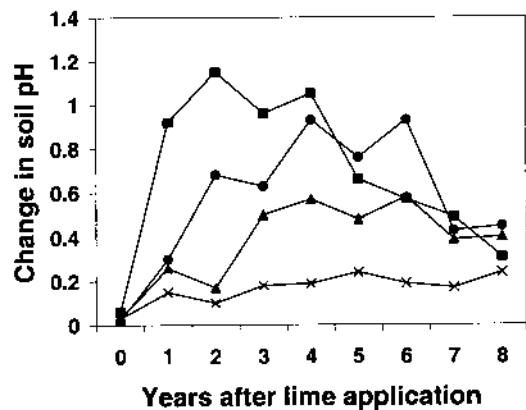
FIGURE 4 Effect of time on the change in soil pH at four soil depths following the application of lime (5 tonnes ha^{-1}); 0–50 mm (squares), 50–100 mm (circles), 100–150 mm (triangles), 150–250 mm (crosses). (Modified from Ref. 70.)

given sufficient input of lime and, significantly, sufficient time. This conclusion is not new and supports the view recorded by Adams [5] that one obvious solution to subsoil acidity is topsoil liming. It is also noted that anthropogenic acidity can occur over small depths within the topsoil [46], well within the reach of surface-applied ameliorants.
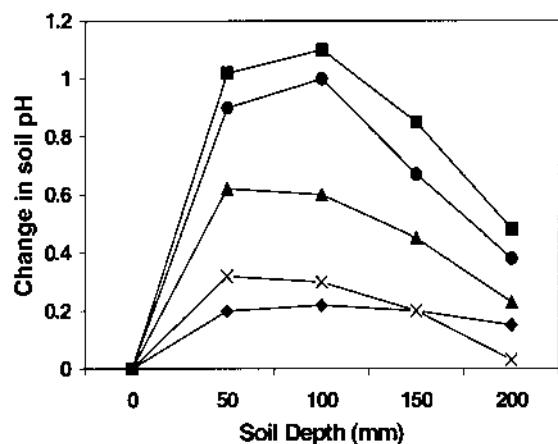
FIGURE 5 Effect of rate of lime application on the change in soil pH at four soil depths. Rates of lime (tonnes ha^{-1}); 10 (squares), 7.5 (circles), 5.0 (triangles), 2.5 (crosses), 1.25 (diamonds). (Modified from Ref. 49.)

Several qualifications are, however, required. If the mechanism by which liming affects the subsoil is chemical [40], then this conclusion requires that there are no long-term impediments to the vertical flow of water through the soil to carry by mass action the soluble products of liming—CO_3^{2-}, HCO_3^-, and OH^-.

Lime in excess of that required to neutralize the surface or topsoil acidity is required for amelioration of subsoil acidity. Sumner [40] suggested that the topsoil pH would need to be well above 5.6 for a sufficient amount of mobile alkalinity to be present. This is certainly consistent with the measurements made by Wheeler and Edmeades [72]. They found that the pH of the soil solution 2 years following the application of lime (7.5 tonnes ha^{-1}) was above 7.5 (unlimed 6.4) and the bicarbonate concentration was about 20 μM (unlimed 2 μM). Sumner [40] also noted that soils with variable charge minerals in their subsoils would consume more alkali than soils with predominantly permanent charged minerals.

Sumner [40] suggested that the rate at which alkalinity moves into the soil may be related to whether Ca and Mg or Na was accompanying the alkali anions. It is interesting to note that Na rather than Ca or Mg is the dominant cation in most soil solutions [17].

The question of where lime should be placed reduces to one of time. Based on first principles, the time required will depend on (1) the amount of water passing through the topsoil, (2) the concentration of alkalinity in the topsoil, (3) the relative concentrations of accompanying cations, (4) the presence of macropores, and (5) the presence of burrowing soil fauna such as earthworms.

If time is of little consequence, as is the case when land is still relatively productive and lime is required simply to offset the current rate of acidification and maintain the current top and subsoil pH, then there is little purpose in doing other than applying lime to the surface. If cropping, then it is relatively inexpensive to incorporate lime into the topsoil during cultivation. If the cropping program is undertaken using zero tillage, then obviously the lime must be surface applied.

If the acid infertility problem lies below the effective "plow" layer for surface incorporation, there are other options. If there is an urgent need for remedial action, then subsoiling is the only option. Sumner [40] has reviewed the various techniques and results. He concluded that the evidence showed clear benefits to deep liming in terms of subsequent root proliferation and hence yield but questioned the practice on economic grounds.

Farina et al. [50] have reported the results of a long-term experiment (11 years) comparing various strategies for ameliorating subsoil acidity. A summary of their results is given in Table 8. Economic analysis (Fig. 6) showed that the best lime incorporation treatments, in terms of plant responses, were cost effective in the long term. Appreciating that such analyses are specific at a regional and crop and possibly site level, they are nevertheless important in the general context because they challenge conventional wisdom. More long-term trials of this nature are required so that the biological basis for long-term economic analysis can be as-

TABLE 8 Long-Term (11 Years) Effects of Incorporation of Lime on the Yield of Corn Grain

Treatment	Yield (tonne ha^{-1}) of corn grain and silage (mean over 11 seasons)
Conventional moldboard incorporation (10 tonnes lime ha^{-1} to 25 cm)	5.4
Deep moldboard incorporation (10 tonnes lime ha^{-1} to 50 cm)	6.2
Gypsum (5 tonnes ha^{-1}) incorporated to 25 cm after conventional moldboard incorporation (10 tonnes ha^{-1} to 25 cm)	6.7

Source: Adapted from Ref. 50.

sessed. It is noted, however, that deep liming with lime incorporation is common practice on very acid peat soils [22,73].

If time is not a factor, then many cases of subsoil acidity could be solved by initial high capital inputs of lime to the topsoil followed by maintenance inputs as discussed earlier. The long-term economics of this strategy have yet to be investigated, and it is likely that the biological information required for such an assessment is also not available.
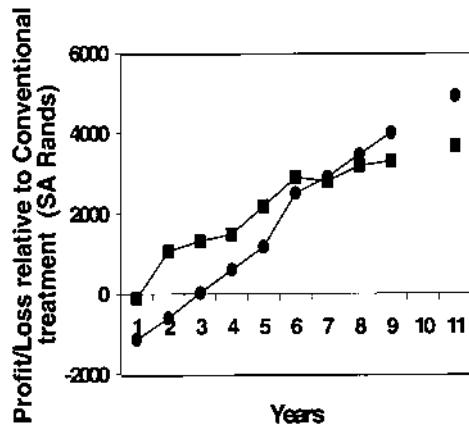
FIGURE 6 Effect of deep moldboard lime incorporation (10 tonnes ha^{-1}, 50 cm, squares) and surface incorporation of gypsum (5 tonnes ha^{-1}, 25 cm, circles) on annual profit or loss from corn grain, relative to conventional moldboard incorporation (10 tonnes ha^{-1}, 25 cm) (no data were collected in year 10). (Modified from Ref. 50.)

Other options such as the use of gypsum or changing land use are beyond the scope of this chapter.

3.3.3 Longevity of the Liming Effect

The traditional liming strategy is to apply sufficient lime in a single application to achieve a specified target pH and to reapply further lime when required. In practice, this is normally determined by monitoring the pH over time. But the economics of liming are very dependent on the duration of the effect on plant production. It is desirable therefore to be able to predict the duration of the effects of liming. Once again, despite the importance of this factor, very few data are available.

Black [2] cites an example from a field trial in the UK showing the effect of time after liming on the soil pH. Edmeades et al. [22] used data like this from long-term trials in New Zealand to model the duration of the liming effect based on rainfall and the rate of application. The higher the rate of application and the lower the rainfall, the longer the duration. For example, the effects of surface application of 2.5 tonnes ha^{-1} lime were given by

Duration (years) $= 9 - [0.0012 \times \text{annual rainfall (mm)}]$

Thus, the duration is about 8 years at 500 mm annual rainfall, decreasing to 6 years at 2000 mm. These figures generally agree with practical experience in New Zealand and in Victoria, Australia.

Symth and Cravo [74] related the Al saturation of the soil, expressed as the proportion of effective cation exchange capacity (ECEC), to the rate of application of lime (r) and time (t) since application, based on trials from Brazil. Aluminum saturation decreased with an increasing rate of lime application and increased with time according to the relationship

Al saturation $= 58.3 - 20.2r + 1.6r^2 + 2.1t + 1.1t^2$

Dierolf et al. [57] subsequently validated this relationship with data from other trials whose duration ranged from 40 to 68 months.

Hockman et al. [37] used a different approach and calculated the residual value of lime based on observed rates of reacidification in the field after liming. They related the pH at time (t) to the initial virgin soil pH (pH_v) for a soil with a buffer capacity (BC_s) according to the relationship

$pH_v = 2.42 + (pH_v - 2.42) \times e^{-0.0058 \times t \times BCs}$

Like field buffer capacity, the duration of the effect of liming is a vital piece of information required to make liming decisions. Hence, more long-term trials are required. Also, if it is assumed that the duration of the effect of lime on plant growth will be related to its effect on pH, such trials need not be expensive to conduct.

3.3.4 Quality of Lime

There are three important components to lime quality—lime equivalence or neutralizing value, particle size, and hardness—the latter being determined largely by the chemical composition of the lime. The impact of these three factors on the effectiveness of liming materials is reviewed elsewhere [2,75], and Goulding and Annis [38] provide a recent summary of research in Britain.

Conyers et al. [76], working with 12 liming materials from NSW, Australia, defined the relative physical efficiency (essentially the particle size) and the relative chemical efficiency (lime equivalence and chemical composition). They found good agreement between the measured and actual total efficiency (the product of the physical and chemical efficiency) as measured in the field.

Although lime quality can vary considerable from location to location, transport costs normally dictate the choice of lime. In any case, a fine, soft, fast-acting lime will have a shorter residual effect than a coarser, harder material. The key is to match the lime quality with the intended use. Many products will be suitable if required for a maintenance program. A fast-acting lime is required where there is an urgent need to increase the soil pH.

3.4 The Economics of Liming

The economics of liming depend on the size of the benefits accruing from liming relative to the cost of liming. The benefits are a function of the size and value of the plant response plus the duration of the liming effect. The costs include the purchase, transport, and spreading of lime.

A cost–benefit analysis can readily be done at an individual site, provided the size and duration of the effect of liming are known, together with the costs. But such information is not transferable to another site unless the size and duration of the plant response to liming can be predicted. In essence, what are required are the production functions for different crops relating the degree of soil acidity, whether measured as soil pH or some other criteria, to the size and duration of the likely plant response.

Slow progress is being made to this end. Edmeades et al. [22] found relationships between soil pH and the size of pasture responses to lime, applied at three rates. This information, coupled with a simple model to predict the duration of pasture responses to liming from the rainfall data, forms the basis of the econometric lime model, the AgResearch PKSLime Program (NZ Pastoral Research Institute Ltd), currently used to offer advice to farmers.

Results are reported, for a given set of farm input data, in terms of the net present value (NPV—the sum of the annual financial benefits per year, for the duration of the response, expressed in current dollar terms) for each potential rate of lime application. The combination of soil pH and stocking rate for which the NPV is positive (liming economic) or negative (liming not economic) is shown in Fig.
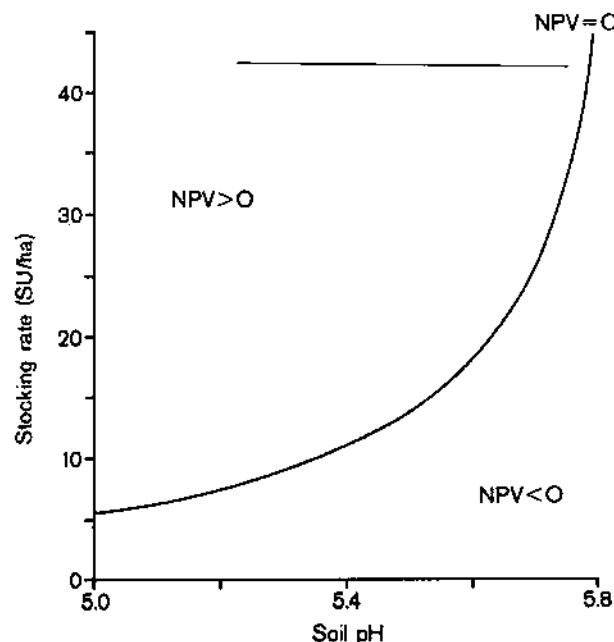
FIGURE 7 Combinations of initial soil pH and stocking rate (stock units ha^{-1}) on sheep farms for which the net present value (NPV, NZ\$ ha^{-1}) for a rate of application of lime is zero. (From Ref. 29. Copyright 1985, SIR Publishing, The Royal Society of New Zealand.)

7. For this set of input data, it would not be economic to use lime if current soil pH is greater than 5.5 and the stocking rate <10.

Similarly, in Australia, Hochman et al. [60] have developed a decision support software system (DSSS) called "Lime-It." In this case, the important production functions are the relationships between soil pH and relative yield for a number of different crops and pastures.

Dierolf et al. [57] have reported the development of an Acidity Decision Support System (ADSS). This is being developed for highly weathered mineral soils for which the sole factor limiting plant growth is Al toxicity. The production functions are the relationships between crop yield and the degree of Al saturation in the soil.

Hochman et al. [60] emphasized the importance of the ratio of the cost (of lime) to value (of the agricultural product) in determining the economics of liming (Table 9). In countries and farming enterprises where the cost/value ratio is low, such as for corn in Alabama, potatoes in The Netherlands, and dairy pastures

in New Zealand, liming acid soils can be highly profitable. In contrast, for enterprises such as livestock production and to a lesser extent cereal cropping in southern Australia, liming is economic only under certain circumstances and often requires excellent management skills in other aspects of the farming enterprise to be so. To some extent, these data explain why the use of lime is more prevalent in some countries than in others.

Undoubtedly, the cost/value ratio does affect the economics of liming, but this masks the most important determinants—the size and duration of the plant response to liming. This is illustrated in Fig. 8. Using the AgResearch PKSLime Program, the effect of altering the cost/value ratio (by adjusting the cost of transporting the lime from NZ$10 to NZ$100 per tonne) on the NPV of liming on an average dairy pasture in New Zealand has been determined at two different lime response levels—2 to 3% and 10 to 12%. In this case, the size of the response, determined by the initial soil pH, has a major influence on the economic outcome. Given that the sizes of many reported crop responses to liming are much greater

TABLE 9 Cost of Lime as a Fraction of Product Value for Various Crops and Locations (Adapted from Hochman et al. [60])

Crop	Location	Value production (US$ ha^{-1} year^{-1})	Cost of lime at 2.5 t ha^{-1}	Cost/value ($\times$100)
Alfalfa (for hay)	Mayfield, Kentucky	260	33	12.7
Soybean	Crossville, Alabama	595	33	6.5
Corn	Southern Coastal Plain, Virginia	740	33	4.5
Winter wheat	Central clay area, Netherlands	3551	380	10.7
Potatoes	Central clay area, Netherlands	9450	380	4.0
Dairy pasture	Volcanic ash soils, New Zealand	460	42	9.1
Sheep pasture	'Easy Hill Country', King Country, New Zealand	300	71	23.7
Pasture for sheep	Southern slopes, New South Wales, Australia	211	150	71.1
Wheat	Wagga Wagga, New South Wales, Australia	264	150	56.8

Source: Adapted from Ref. 6.0.
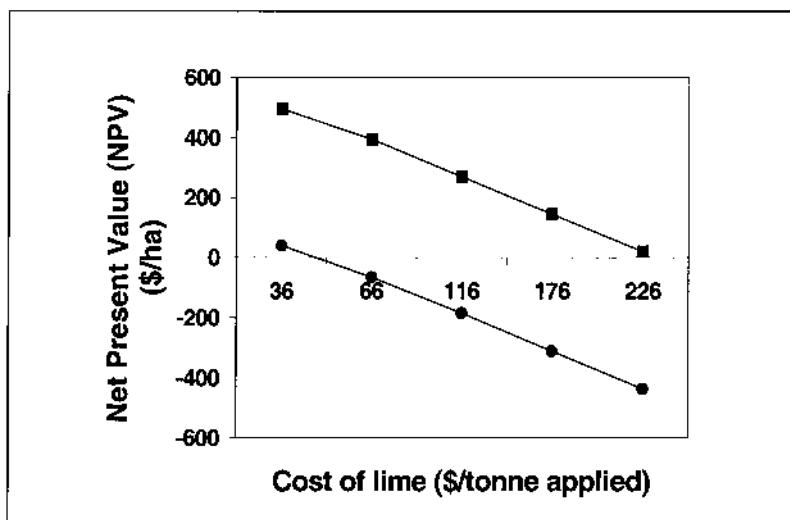
FIGURE 8   Effect of total cost of lime (product, transport, and spreading) and size of response to lime (2%, circles, and 10%, squares) on the net present value (NPV, NZ\$ ha^{-1}) for an average dairy farm in New Zealand (gross margin NZ\$600 ha^{-1}).

than used in this example (Table 4), it is surprising that liming is so frequently dismissed as uneconomic.

Similarly, the duration of the response (Sec. 3.3.2) also has a major impact on the economic outcome of liming. The reason for this is that the initial one-off cost of liming is spread over the duration of the response to liming. In New Zealand, this can range from 4 to 10 years.

Given their importance in determining the economic outcome of liming, more basic research is required to define these parameters across the range of soils and crops of economic value. Until such work is done, it should not be asserted that liming acid soils is not economic and that, therefore, the only solution to acid soil infertility is to find other nonliming remedies (for example, see Ref. 46). This will require a change in attitude and hence science direction.

3.5   Social Issues

Lime is most commonly applied on acid soils in industrialized countries [77]. It is technically and economically feasible to lime acid soils in such countries. But in other countries, the successful management of acid soils depends upon integrating the technical issues with social and economic factors [62]. Social factors can be pivotal reasons why some people may choose not to lime before even considering

economic or biophysical factors. Issues such as land tenure, culture, history, attitudes, values, knowledge, learning, and access to information can be important social considerations.

3.5.1 Land Tenure

Land tenure is an issue with respect to decisions about liming. This arises because the effects of liming can be slow and it can be many years before the benefits of liming are fully realized. Where people have stable land tenure, they can make sensible long-term decisions about acid soil management, including liming, farming the least acid areas, or choosing acid-tolerant plants [78]. If land tenure is in doubt, the decision regarding lime use is largely irrelevant because of the uncertainty in recouping the cost of the investment.

3.5.2 History, Culture, Attitudes, and Values

In many European countries, the United States, and New Zealand there has been a long history and ingrained belief that liming acid soils is the "right thing to do" (see Refs. 79–81 for examples). The situation in Australia provides an interesting contrast because, until recently, it had limited liming culture. The use of lime was not part of its culture. This has had, and we suggest, will continue to have, a significant impact on how acid soils are considered in Australia and how the problem is to be resolved.

Consider for example the data in Table 4. Most scientists would agree that these data are consistent with the hypothesis that crop responses to liming are variable and cannot be predicted. The subsequent scientific activities flowing from such a conclusion are likely to follow one of two paths (Fig. 9). Some will progress with the logic that if lime responses are unpredictable, reflecting a complex subject, then the solution to soil acidity is to find alternatives to liming. In following this path, it is likely that they will be predisposed to find reasons not to lime and will review data accordingly. Those who choose the alternative path will set about finding out why lime responses are not predictable and develop the understanding, and hence techniques, to remedy this problem. They will be predisposed to regard liming as the solution to soil acidity. Neither path is right or wrong for both outcomes are potential solutions. The difficulty arises when one's predisposition influences the objectivity with which the whole picture, including data relevant to both potential solutions, is viewed.

The broader cultural setting is likely to influence which path is chosen. This is illustrated by comparing the attributes of agriculture and agricultural research between New Zealand and Australia (Table 10). Given their intensive agriculture, favorable cost/product ratio, and an inherited prolime culture from Europe, it is not surprising that New Zealand has embraced the "lime is the solution" path. From early days, scientists have supported the use of lime and been encouraged to develop the appropriate diagnostic criteria and solutions. Only subsequently have
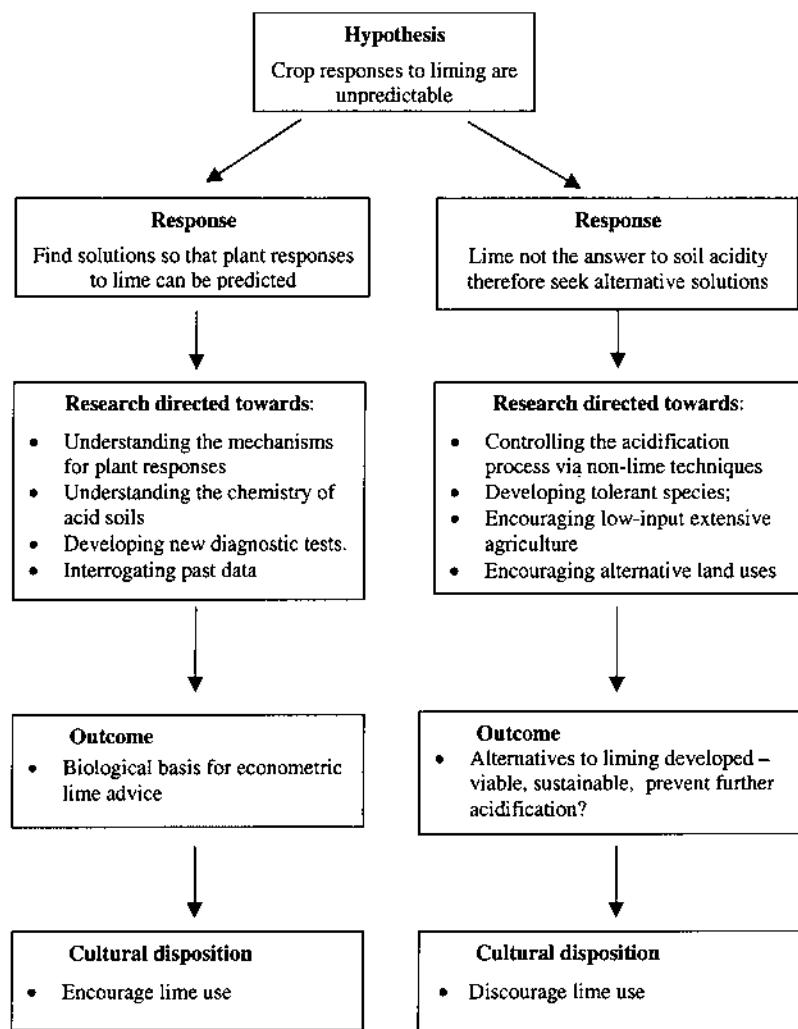
FIGURE 9 Schematic diagram showing the possible conclusions and responses to the hypothesis that crop responses to liming are unpredictable.

the New Zealand scientists concerned themselves with the other nonliming options such as managing the rate of acidification and plant tolerance to acidity.

In contrast, but with equally compelling logic, scientists in Victoria, Australia, have moved increasingly down the alternative path. For them, understanding the processes of ongoing acidification, in the hope of alleviating its impact, and the development of acid-tolerant plant material was the priority.

Problems arise when the path is set because any new issues, or interpretation of existing data, are examined through a mind set consistent with a cultural predisposition. An example of this is that one of the current authors (DCE) looks at the data in Table 4 and sees enormous opportunities, whereas the other (AMR) sees many insurmountable problems!

Other examples demonstrating the effect of cultural predisposition are highlighted in this chapter. The attitudinal difference between the soil chemist and the agronomist with respect to defining the optimal soil pH has now been resolved. Further time will be required before everyone will readily and without resistance distinguish between the soil lime requirement and the biological lime requirement.

Our reinterpretation of the data in Table 7 is a consequence of path-one thinking, as is our interpretation of Fig. 8. So too are the conclusions reached by Farina et al. [50] with respect to the economics of subsoiling (Fig. 6). Of course,

TABLE 10 Case Study Comparison of the Physical, Economic, and Cultural Differences Between Pastoral Agriculture in New Zealand and Victoria, Australia[a]

Dimension	Attribute	New Zealand	Australia
Physical	Rainfall (mm year^{-1})	600 to 2000	600 to 1000
	Land value (AU\$ ha^{-1})	1200 to 10000	1000 to 1500
	Stocking rate (stock units ha^{-1})	5 to 30	5 to 25
	Soil pHw	5.0 to 6.2	4.6 to 5.6
	Response to lime (%)	0 to 10	0 to >100
Economic	Gross margin (AU\$ ha^{-1})	150 to 800	100 to 400
	Lime cost (AU\$ ha^{-1} on ground)	24 to 32	60 to 70
	Cost/output ratio (lime cost/gross margin $\times$ 100)	4 to 20	16 to 64
Cultural	Historical farming practices	Conservative	Exploitive
	Financial survival strategy	Intensification Increase production per unit area	Extensification Increase land holding
	Sustainability strategy	High input–output maximize efficiencies	Low input minimize costs

[a] Figures are generalized for the purpose of this comparison and should not be interpreted to indicate the financial viability of either system.

both approaches are required to solve the worldwide soil acidity problem, and to that end, a dispassionate, objective assessment of past lime research and future research needs is always required.

3.5.3 Knowledge, Learning, and Access to Information

Local knowledge is very important in making decisions about management of acid soils. An important farmer's strategy has been to select, where possible, soils less constrained by acidity and to use acid-tolerant plant varieties [78]. This works where there is sufficient land available [62].

Learning is crucial in increasing farmers' knowledge and ability to make informed choices about acid soils and liming. Extension is now developing from a reactive basis, whereby learning is a consequence of exposure to technology, to a program where education and understanding are the prime objective. Effective learning is achieved by doing rather than reading or listening to information. Community extension programs based on small numbers of farmers in their natural social groupings are useful for accelerated awareness and adoption of technology [82].

Better decision making is likely to result from increased access to information, provided the information is used in a discerning manner. Education and training are likely to result in an increased ability to filter appropriate information.

3.5.4 Off-Site Effects

In some situations, the broader off-site impacts and specifically the environmental and hence social impacts may also need to be considered. For example, if liming was practiced on a wide scale and for a long duration in pastoral agriculture in Victoria, Australia, it would be likely that large production increases would result. A commensurate increase in livestock would be required to harvest this production and make the investment economic. Nutrient inputs as fertilizer would also increase to balance the nutrient budget. A consequence could therefore be greater losses of nutrients, particularly N and P, to catchments and waterways.

Thus, improving the quality of the soil resource may adversely affect the quality of the water resource—is this desirable given its impact on the social resource? In such a case, it may be necessary, in the broader social interest, to forgo the value of the soil resource, even though the technology is available to do otherwise.

Such issues are intractable and highlight at the broadest level the theme of this chapter. Liming decisions at the biophysical level, while complex and difficult, can be made objectively provided the principles are clear and the biological data are available. However, such decisions may be different, and indeed irrelevant, within each cultural and social setting.

4 CONCLUSIONS

Much progress has been made in the last 50 years in understanding the nature of the soil–plant acidity complex and how lime can be used to ameliorate the adverse effects of soil acidity. It is now accepted that the old concepts of the ideal soil pH are no longer appropriate and the optimal soil pH and hence the soil lime requirement need to be defined in terms of the plant species and genotypes to be grown. It is also necessary to take into account the specific reason for poor plant performance. For these reasons, it is possible today to be more precise about the amount of lime required for optimal production in specific situations.

The processes that contribute to anthropogenic soil acidification highlight that all soils, not just those that are currently acid, have a requirement for lime or some other source of alkali. In addition, they emphasize the need to consider the fertility of the soil below the plow layer when the issue of soil acidity is considered.

It is possible to define a process for making decisions about lime use so that all components, the soil, plant, and the agricultural system involved, are considered. This highlights the weaknesses in the current body of knowledge. Specifically, the relationships between plant production and soil acidity—the production functions—need to be defined for the whole range of crops. Similarly, there is an urgent need for field-based measurements of soil buffer capacity and the duration of the liming effect on soil properties and plant production.

Together, this information is needed so that the long-term economics of liming can be examined in a systematic and objective manner. This will provide policy makers, planners, scientists, and advisers with a sound biological basis for confidently making lime recommendations. To achieve this, a change in attitude and culture is required, one that sees lime and liming as a solution to the soil acidity problem. However, decisions about lime use must also be considered within the broader social context. This arises because of the diversity in social, agricultural, economic, and environmental systems and constraints imposed on those who use and manage acid soils.

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12

Role of Organic Matter in Alleviating Soil Acidity

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1 INTRODUCTION

The principal adverse effects of acidity on soil fertility occur at soil pH values below 5.5 due to acid dissolution of aluminum (Al) and the onset of Al phytotoxicity to susceptible plants [1]. Aluminum phytotoxicity results in rapid inhibition of root growth due to impedance of both cell division and elongation [1]. This results in reduced volume of soil explored by the root system and direct interference with uptake of ions such as calcium and phosphate across the cell membrane of damaged roots [2]. These phytotoxic effects are unimportant in moderately acidic soils with pH values of 5.5 to 6.5 when the concentration of toxic forms of Al is normally negligible. Manganese toxicity and deficiencies of phosphorus, calcium, and magnesium are common in acidic soils. Soil nutrient deficiencies exacerbate the problem of inefficient nutrient uptake due to restricted root growth and root damage [3]. In drier environments, poor water use due to poor root development is considered to be another adverse effect of Al phytotoxicity.

The best management practice in these Al toxic soils is to treat acidity first because this promotes adequate root growth and function and allows nutrients and water to be taken up more effectively. Both exchangeable Al and Al saturation are used as indices of Al phytotoxicity because these values are dependent on the activity of Al in soil solution due to cation exchange processes. The severity of Al toxicity is directly dependent on the activity of inorganic Al species in the soil solution [4,5]. Organically bound Al species are less toxic [6–8]. Therefore the first objective of acid soil treatment is to decrease the activity of inorganic Al in soil solution. In most agricultural soils, the negative logarithm of the activity of monomeric inorganic Al (pAl) in soil solution is directly proportional to soil pH [9,10]. This simple linear relationship suggests that transient complexation of Al in soil solution by dissolved organic matter and by sulfate additions would not have a lasting impact on Al activity.

The main controlling factor is the soil pH. The direct way to decrease Al phytotoxicity (increase pAl) is therefore to increase soil pH. Lime has been used for thousands of years for this purpose. Large quantities of lime of the order of 1 to 10 tons per hectare are commonly required every few years for adequate crop performance. The slope of the pAl-pH relationship depends on the amount of protons required to dissolve Al from the solid phase. In the case of gibbsite and amorphous aluminum hydroxide, the slope is 3. The intercept is dependent on the solubility of the solid phase, which is greater for amorphous aluminum hydroxide than crystalline gibbsite. Both the slope and the intercept vary in soils; hence, another potential approach is to manage the soil and modify the linear relationship between soil pH and pAl to allow lower Al activity at any given pH value.

Numerous laboratory experiments that have been aimed specifically at measuring the effect of organic matter additions on soil acidity show increased soil pH, decreased Al saturation, and in some cases decreased Al solubility. Occasionally, the opposite happens and organic matter additions result in acidification. The findings of recent experiments have helped us to unravel the mechanisms involved in different types of organic matter. These mechanisms are reviewed here in order to explain the apparently conflicting observations. Our second aim is to show how the knowledge reviewed can be applied to treat soil acidity in farming systems. This approach is particularly important in low-input agroecosystems where high rates of lime cannot be used because of its high cost relative to the value of the farm products. It is also important where alternative, organically based sustainable agricultural practices are being sought.

2 MECHANISMS OF ORGANIC MATTER EFFECT ON SOIL PH

Organic materials that could potentially be used to ameliorate soil acidity include undecomposed plant materials, composts, manures, peats, and coal products. Ad-

ditions of undecomposed plant materials such as prunings to acid soils often result in increased soil pH, decreased Al saturation, and improved conditions for plant growth [11–14]. Similarly, addition of plant residue composts, urban waste compost, animal manures, and coal-derived organic products to acid soils have been shown to increase soil pH, decrease Al saturation, and improve conditions for plant growth [15–18]. The acid-ameliorating properties of farmyard manure and of undecomposed plant materials have been used to improve the yield of corn and beans on an acid Oxisol in Burundi [19]. Composts and manures are mostly derived from waste products that need to be disposed of in a sustainable way in order to avoid environmental pollution. Alkali-treated coal wastes from Victoria, Australia have a similar effect in increasing soil pH [20]. The recycling of these organic waste products for soil amelioration is a double benefit for both the environment and the economy provided that the waste materials are not contaminated with harmful impurities.

The principal mechanisms involved in increasing soil pH vary for organic materials, and a broad distinction can be made between undecomposed plant materials and composts, manures, peat, and coal products. Plant materials undergo decomposition in moist warm soils, and a high proportion of the proton consumption and corresponding increase in soil pH can be attributed to processes associated with decomposition. Composts, manures, peat, and coal products are more stable to decomposition than undecomposed plant materials and contain humic-type substances. The functional groups of these humic substances confer metal binding and pH buffering capacities, which are important in determining the pH of the treated soil. These two broad groups of organic substances are considered separately in order to illustrate the main mechanisms involved during acid amelioration.

2.1 pH Changes Induced by Additions of Composts, Manures, Peat, and Coal Products

Until recently, one of the main problems encountered when considering the use of composts, manures, peat, and coal products to treat acid soils on a routine basis was their compositional variability. This meant that their acid-ameliorating properties were uncertain and the use of these materials for ameliorating acid soils was risky because of insufficient knowledge of the mechanisms involved and unpredictable benefits. Several mechanisms have been postulated for explaining their effect on soil pH. These mechanisms include specific adsorption of organic anions on hydrous Fe and Al surfaces and the corresponding release of hydroxyl ions [16], proton consumption during reduction of metallic ions due to oxygen consumption during decomposition of composts and manures, and ammonification of labile organic N in composts and manures. The proposed liming effect of organic matter adsorption on hydrous Fe and Al surfaces is similar to that of sulfate ad-

sorption [21]. Adsorption of Al by organic matter sites and the subsequent dissolution of the inorganic phase to maintain the equilibrium Al activity in soil solution have also been postulated to increase soil pH [22].

These postulated mechanisms are possible, but their specific individual importance in contributing to pH change has not been evaluated. Composts, manures, peat, and coal products contain humic and fulvic substances with functional groups such as carboxyl groups that are able to consume or release protons according to their pK_a values and the pH of the surrounding solution [23,24]. Progress in investigating the mechanism of acid amelioration experimentally involved the use of strong acid titration to pH 4.0 in order to determine the proton consumption capacity of samples of plant residue compost, urban waste compost, farmyard manure, and peat [22]. Subsequent aerobic incubation of these organic materials with moist samples of an Oxisol from Burundi, Ultisol from Cameroon, and Spodosol from Sumatra resulted in increased soil pH. The increase in soil pH was accompanied by a corresponding decreased exchangeable Al concentration, increased cation exchange capacity (CEC), and hence decreased Al saturation (Fig. 1). The pH of the incubated soils was linearly related to the proton consumption capacities (x, mol$_c$ kg^{-1}) of the organic materials used. This suggests that the major mechanism for increased soil pH is proton exchange between the soil and added organic matter [22]. The regression
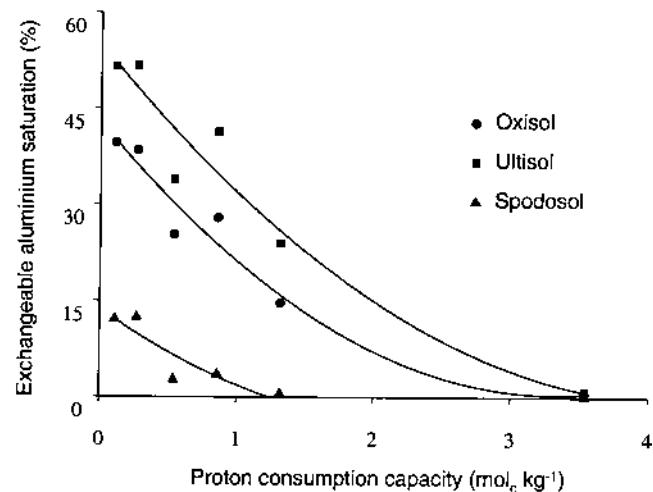
FIGURE 1 Soil exchangeable aluminium following 2 weeks of incubation with 1.5% by weight of organic matter having different proton consumption capacities. (Redrawn from Ref. 22.)

equations for the pH of the incubated soils measured at 14 days of incubation were (Fig. 1)

Oxisol: $\quad$ pH $= 4.51 + 0.29x, \quad r^2 = 0.999$ $\qquad$ (1)

Ultisol: $\quad$ pH $= 4.11 + 0.41x, \quad r^2 = 0.989$ $\qquad$ (2)

Spodosol: $\quad$ pH $= 4.06 + 0.61x, \quad r^2 = 0.991$ $\qquad$ (3)

The constants of these linear regression equations were close to the pH values of the untreated soils. The slopes were indicative of the soil buffer capacity, the Oxisol being most strongly buffered and the Spodosol least buffered.

In order to test further that the increase in soil pH was due to the flow of protons from the soil to the organic matter sites, the pH of the incubated treated soil was predicted by plotting the buffer curves of both the organic material and the soil simultaneously (Fig. 2). The intersection of the two buffer curves predicted the incubated soil pH with good accuracy, confirming that the major process responsible for the increase in soil pH is simply proton exchange between the soil and added humified organic material. This work allows prediction of the treated soil pH that is valid across soils as well as providing an effective means of addressing the issue of variability in the composition of humified organic materials used in the treatment of soil acidity [22]. The treated soil pH can be predicted from
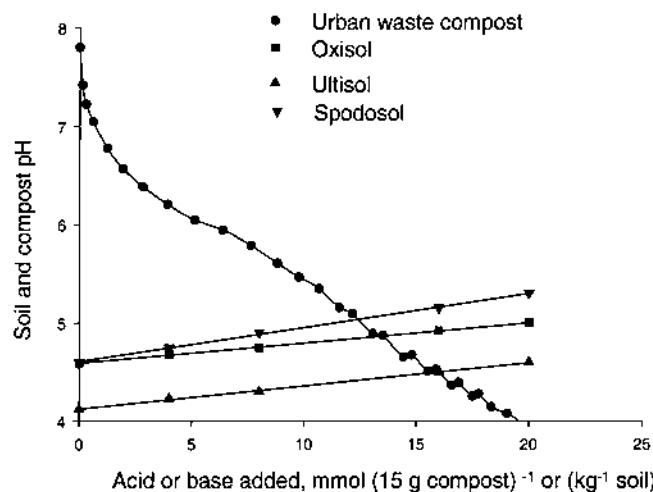
FIGURE 2 Example of the initial pH and buffer characteristics of one organic material (urban waste compost) and the incubated soils. The pH buffering is shown for 1 kg soil and 15 g compost used during incubation. (Redrawn from Ref. 22.)

(1) the initial pH of soil and organic matter and (2) the buffer characteristics of soil and organic matter. The soil buffer characteristics should be relatively stable over a period of a few years and therefore, on a routine basis, only the soil and organic matter pH and the organic matter buffer characteristics are required. The increased soil pH leads to a corresponding increase in cation exchange capacity and decrease in Al saturation.

The implications of proton flow from the soil (lower pH) to the organic matter (higher pH) buffer systems as the main mechanism of acid amelioration is that, if the soil pH is higher than the organic matter pH, a decrease in soil pH will be measured due to flow of protons from lower pH (organic matter) to higher pH (soil). For example, application of sewage sludge compost with a pH value of 6.4 to a soil with a pH value of 7.7 resulted in decreased soil pH [25]. An important additional reason for a subsequent decrease in soil pH is further decomposition of less stable materials in the soil resulting in mineralization and nitrification of organic nitrogen. Using poultry litter and litter compost, Tyson and Cabrera [26] showed that there was an immediate increase in soil pH that could be attributed to proton flow from the soil. The soil pH increased further during incubation due to ammonification and peaked at 7 days of incubation. The soil pH then decreased to levels below those of the untreated control because of nitrification, which releases $2H^+/NH_4^+$, compared with ammonification, which consumes only $1H^+/NH_4^+$. The uncomposted litter had lower pH values than the composted litter due to larger amounts on nitrogen being nitrified. This nitrogen-led increase in soil pH is transient, and nitrification of organic N is expected to acidify the soil. The proton flows or alkalinity production associated with ammonification by deamination [Eq. (4)] and urea hydrolysis [Eq. 5] and with nitrification [Eq. (6)] are as follows:

$$R\text{—CH (NH}_2)\text{—COOH} + 3H^+ + 2e^- \rightarrow R\text{—CH}_2\text{—COOH} + NH_4^+ \quad (4)$$

$$CO(NH_2)_2 + 3H_2O \rightarrow 2\,NH_4^+ + 2OH^- + CO_2 \quad\quad\quad\quad\quad (5)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad\quad\quad\quad\quad\quad\quad (6)$$
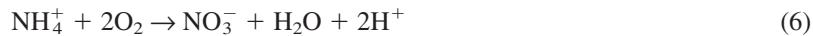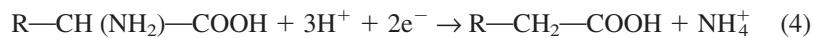
The net longer term effect of addition of this type of more reactive nitrogen-rich organic manure is therefore expected to be determined by the balance between its proton consumption capacity and acid production by processes such as nitrification. Materials with high acid consumption capacities and low mineralizable nitrogen content would be more effective than materials with low acid consumption capacities and high nitrifiable nitrogen content.

2.2   Effect of Undecomposed Plant Materials on Soil pH

An initial increase in soil pH often occurs immediately upon addition of plant materials to acid soils [27]. This is a chemical process that is independent of biological activity [28]. Examination of the data presented by Tang and Yu [28] for five soils incubated with 10 plant materials shows that increased soil pH generally oc-

curred when the initial soil pH values were lower than those of the plant residues. Soils with pH values greater than those of the residues generally suffered a decrease in soil pH after treatment. This suggests that the mechanism postulated earlier for humified materials also applies for plant residues when microbial decomposition is absent. In these situations, the amount and direction of flow of protons between the soil and organic matter buffer systems dictate the direction of pH change; for very acid soils, an increased soil pH is normally observed. Following this immediate increase in soil pH, incubation of soil treated with plant residues under nonsterile conditions results in further increases in soil pH as a result of microbial activity.

The time course of soil pH during moist, warm incubation is varied and typically shows an increase to a maximum reached in 8 to 147 days, depending on the plant materials, amounts applied, and the soil properties [29,30]. This fluctuation gives rise to time-dependent relationships between the treated soil pH and plant residue composition [30]. These changes occur as a result of processes related to organic matter decomposition. Materials rich in organic nitrogen such as soybean leaves (29 g N/kg, C/N $\sim$ 17) and barley grain (28 g N/kg, C/N $\sim$ 18) result in a more pronounced peak than materials such as wheat straw with 5 g N/kg and C/N $\sim$ 100 [29]. Comparisons of the pattern of pH change by plant materials with fully characterized model organic compounds suggest that ammonification of organic nitrogen in the plant residues is an important contributor to the pH increase to the peak values due to proton consumption [Eq. (4)]. The rate of ammonification of organic N depends on the C/N ratio of the plant materials and their lignin and polyphenol contents. The rate of ammonification is expected to be slow when the C/N ratio is >30. This ratio narrows during decomposition and results in increased ammonification rates. A subsequent decrease in soil pH occurs after ammonification due to nitrification of the ammonium ions and the release of 2 moles of protons per mole of ammonium. In the case of barley grain, which has a low base cation content of 256 mmol$_c$ kg^{-1}, nitrification causes the pH to fall to that of the untreated soil. The effect of ammonification is therefore transient [29]. This nitrogen-led pH fluctuation is less important with low-nitrogen residues [14,27].

An important and longer lasting cause of pH increase during incubation is microbial decarboxylation. This results in consumption of 1 mole of protons per mole of carboxyl [Eq. (7)]. The effect of decarboxylation on proton consumption can be illustrated with calcium oxalate [31]:

$$Ca(COO)_2 + \tfrac{1}{2}O_2 + 2H^+ = 2CO_2 + H_2O + Ca^{2+} \tag{7}$$
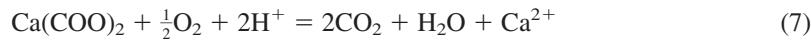
A good correlation is therefore obtained between the soil pH increase and the amount of carbon dioxide evolved during incubation of soil treated with organic anions [32]. According to Eq. (7), the amount of alkalinity associated with calcium mineralized from the simple organic molecules has the same liming effect as the amount of alkalinity associated with calcium found in lime; in each case

$2H^+/Ca^{2-}$ are consumed during acid neutralization. The reaction is, however, slower than that with lime because decomposition is involved. The neutralization process is quicker with materials with a higher nitrogen content, which increases the rate of decomposition [29]. With plant materials, calcium is present with additional base cations such as magnesium and potassium. The sum of charge carried on these base cations is closely related to the ability of undecomposed plant materials to neutralize soil acidity [29,30]. This cation charge is related to ash alkalinity of the plant material measured by titration of its ash [33]. For example, incubation of an Oxisol and an Ultisol with prunings from seven agroforestry tree species with base cation content (b, cmol$_c$ kg^{-1}) increased soil pH measured at 14 days [30]:

$$Oxisol \qquad pH = 5.61 - 1.58b + 0.77b^2, \qquad r^2 = 1.00 \qquad (8)$$

$$Ultisol \qquad pH = 4.23 - 0.74b + 0.62b^2, \qquad r^2 = 0.95 \qquad (9)$$

The pattern of soil pH during incubation with plant materials is due to a combination of the transient effect of ammonification, the reversal of the ammonification effect by nitrification, and the release of alkalinity by the decarboxylation process. These processes are governed by the chemical composition of the plant materials. In addition to the chemical composition, the time course of soil pH during incubation is dependent on the soil type (Fig. 3). The pH of the treated Ultisol measured at 42 days was higher for all treatments than that measured at 14
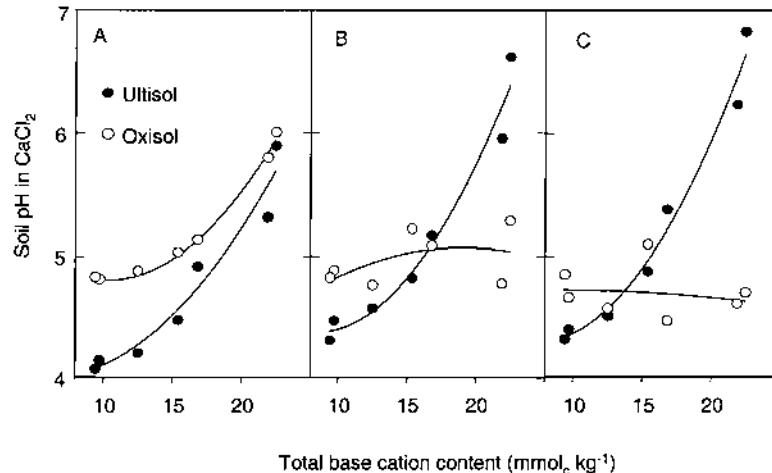
Figure 3 Effect of total base castion content of tree pruning on soil pH in an Oxisol and an Ultisol measured at (A) 14, (B) 42, and (C) 98 days of incubation. (Redrawn from Ref. 30.)
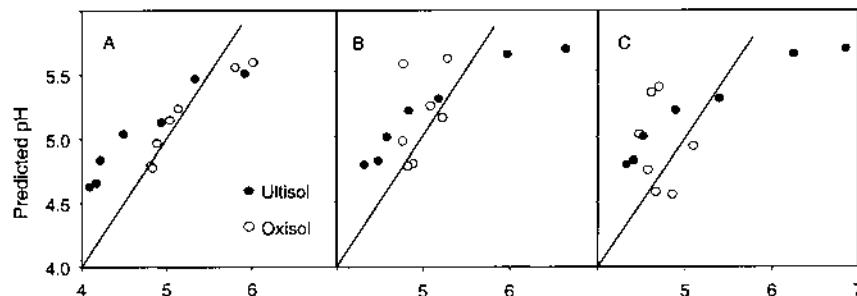
FIGURE 4 Comparison of the measured and expected soil pH in an Oxisol and an Ultisol after (A) 14, (B) 42, and (C) 98 days of incubation assuming that the net acid-neutralizing capacity of each pruning addition is equal to its base cation charge. The 1:1 line is given for reference. (Redrawn from Ref. 30.)

days, but was the same as that measured at 98 days. In this soil, the total base cation content remained a good predictor of the pH of the treated soil throughout the 98-day incubation period. In contrast, the pH reverted to lower values after a 14-day incubation in the Oxisol. Comparison of the effects of lime with those of the base cations present in the plant materials showed that with the Oxisol, the base cations were as effective as lime when measured at 14 days. A similar relationship was obtained for the Ultisol at 42 days, suggesting that in both cases the base cations were as effective as lime in acid amelioration. This is in accord with measurements made for the decarboxylation of simple nitrogen-free organic molecules. In the case of the plant materials, the presence of nitrogen meant that the measured pH values deviated from those achieved by using lime (Fig. 4). The Oxisol had a higher organic carbon content (45 g C/kg) than the Ultisol (26 g C/kg); this is expected to lead to more rapid decomposition of the pruning materials because both soils had similar clay contents [34]. It is feasible that further nitrification may decrease the pH of the Oxisol below that of the untreated control after 98 days. In another soil, the liming effect persisted as long as 574 days [29]. The duration of acid amelioration is therefore long enough to provide a window for crop growth in soils that are normally Al toxic. The decarboxylation process results in a change in the buffering properties of the soil from more strongly acidic to weaker acidic functional groups, resulting in stronger retention of protons [27].

The current trend is to rank the acid amelioration value of plant materials according to their total base cation content because this property is related to their longer term effect following the transient effect of ammonification. Total base cation content can be estimated from published tabulations of leaf nutrient levels, e.g., Drechsel and Zech (35) for broad-leaved tropical trees. Because the total base cation contents are deemed to have the same amount of alkalinity as the cation

content of lime, relatively large additions are required because of the low base cation content compared with lime. This ranking is a first step because the temporal patterns of acid amelioration achieved by different plant materials are different and field experiments showed that the ranking of plant materials measured in the laboratory did not match that measured in the field [36]. Additional processes, such as leaching and crop uptake of nutrients, further complicated the prediction of acid amelioration.

3 DECREASING AL SOLUBILITY BY MODIFYING THE RELATIONSHIP BETWEEN PH AND PAL

The activity of Al^{3+} in soil solution of mineral soils is often described by using the solubility of an aluminum hydroxide phase such as natural gibbsite as follows:

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \tag{10}$$

$$\frac{[Al^{3+}]}{[H^+]^3} = \text{constant} \tag{11}$$

$$\log Al + 3pH = \log k \tag{12}$$

The value of $\log k$ at 298 K varies from 8.11 to 8.77 depending on the solubility of the mineral phase in soil. The slope of the relationship between $\log Al$ and pH is 3. This approach often overestimates the activity measured at pH <5.0. In addition, the cubic relationship between pH and pAl is often not observed. The undersaturation has sometimes been attributed to kinetic constraints to mineral dissolution. Although this may occur in some soils, there is increasing evidence that at low pH values, organic matter Al complexes control the activity of Al in soil solution [37–41]. This allows acid soils with high organic matter content or soils amended with organic matter to have low soil solution Al concentrations and to grow good crops under conditions that would normally exhibit Al toxicity.

The relationship between pAl and pH is also normally linear at the natural acid soil pH values when organic matter Al complexes control the activity of Al in the soil solution. The slope is often <3. In some North American soils, the slope could be predicted from its linear relationship with the bound Al ratio. This ratio is determined by extracting organically bound Al with $CuCl_2$ and is defined as the equivalents of Cu-extractable Al per unit organic matter divided by the equivalents of carboxyl groups per unit organic matter [37]. The intercept is inversely proportional to the bound Al ratio. As the bound Al ratio decreases, Al solubility also decreases provided that soil pH <5.0 because the organic-Al and $Al(OH)_3$ solubility lines intersect at about this pH value [37]. Further work on a larger range of O horizon samples of Spodosols, Alfisols, Ultisols, and Inceptisols showed that average values of slope and intercept based on the bound Al ratio could be used [39]. The equilibrium Al activity was reached within a 48-hour period. It is un-

likely that the observed undersaturation was due to kinetic restriction of dissolution of the $Al(OH)_3$ phase as is sometimes postulated.

Further work by Mulder and Stein [42] and Wong and Swift [43] suggests that the often-measured undersaturation is due to the control of Al activity by organic matter–Al complexes rather than slow dissolution of the mineral phase. Organic matter–Al complexes have also been found to control Al activity in the mineral soil layer and account for the apparent undersaturation with respect to $Al(OH)_3$ [38,40,42,43]. A decrease in Al solubility was observed with decreases in the ratio of organically bound Al to total soil organic carbon. The bound Al ratio also controls the nature of the relationship between pH and pAl, which becomes increasingly curvilinear as the ratio increases. Linear regression is simple, easy to use, and adequate in many situations, but it appears to be unsatisfactory at a bound Al ratio >0.7 and outside the pH range of 3–5 because deviation from linearity increases at very low pH values and at pH >5 the gibbsite equilibrium appears adequate in modeling the soil solution Al activity. This nonlinear behavior can be predicted with more generally applicable mechanistic chemical equilibrium models such as Windermere humic aqueous model (WHAM), which considers specific and nonspecific ion binding by humic substances [41].

Increasing total soil carbon with organic matter additions increases the carboxyl content and CEC. This can also decrease the bound Al ratio. Artificial addition of humified organic matter to acid subsoil has been shown to decrease the concentration of Al at any pH values compared with the untreated soil [44]. This decrease in Al concentration was accentuated with increasing additions of organic matter. The lowered aluminum concentration allowed barley to grow better in organic matter–treated acid soil than the untreated control at the same pH values [44]. The activity of Al in soil sampled from the A horizon of an Oxisol from Burundi and an Ultisol from Cameroon was undersaturated with respect to the solubility of natural gibbsite. Wong and Swift [43] postulated that the undersaturation was due to the control of soil solution Al by organic matter–Al complexes and showed that Al solubility could be decreased further in these mineral soils by additions of organic matter. The organic matter treatment lowered the solubility of Al, giving rise to lower Al activity in solution at any given pH in the range of 3.3 to 4.8. The treatment did not change the slope of the solubility lines measured at 12 and 28 days of incubation. In the Oxisol only, the slope increased from 2.16 to 2.74 at 35 days of incubation. The treatment continued to have no effect on the slope measured at 35 days of incubation for the Ultisol. These A-horizon samples therefore appear to behave differently from the O-horizon soil samples used by Cronan et al. [37]. The decreased Al solubility with humic acid treatment led to a corresponding decrease in Al saturation [43]. Soil incubation with plant residues appears to have a similar effect, and over a range of pH values the concentrations of monomeric Al found in the residue-treated samples were generally lower than those of the samples treated with lime [33]. This effect would decrease the soil pH

at which Al phytotoxicity occurred. The effect of organic matter on Al solubility could explain earlier observations that at the same pH values, higher soil organic matter content corresponded to lower exchangeable Al concentrations [44,45]. The opposite—an increase in Al solubility at a given pH—is observed when lime is used because of the formation of more soluble freshly precipitated Al hydroxide [10].

Increased uptake of Al is often observed as the soil pH value is increased from 5.5 to the neutral value. Farina et al. [46] observed a corresponding decrease in crop yield in an Oxisol and an Ultisol containing 6.6 and 3.2% organic matter. This effect is less pronounced in subsoils than in the corresponding topsoil samples [47] but is more pronounced in soil that has been treated with organic matter [44]. This increased uptake of Al at the near-neutral soil pH may be due to increased solubility of Al–organic matter complexes in that pH range [48]. The solubility line for organically bound Al crosses that of soil $Al(OH)_3$ at about pH 5.5. The soil solution will maintain oversaturation with respect to natural gibbsite above this pH value until amorphous $Al(OH)_3$ is precipitated [39]. The presence of organic matter in soil solution would interfere with this precipitation and favor oversaturation by Al [49].

4   AMELIORATION OF SUBSOIL ACIDITY

Subsoil acidity occurs below the depth at which lime can be incorporated by "normal" cultivation methods so that amelioration relies on the slow movement of lime or the use of more mobile amendments such as gypsum and soluble organic matter. Naturally occurring and agriculturally generated subsoil acidity limits root growth and hence nutrient and water uptake by susceptible crops at depth and is a threat to the sustainability of agriculture in many regions throughout the world [50–52]. The use of lime to treat subsurface acidity has met with varied success because of its low solubility in acidic to neutral soil conditions, giving rise to variable mobility of lime alkalinity down the soil profile [53]. Downward movement of lime is a function of soil type, rate of addition, soil pH, and rainfall and is feasible in sandy soils [52], whereas in more heavily textured soils, physical deep incorporation of lime into the soil profile is needed [50]. This practice is costly and may not be economic in many places. Gypsum and phosphogypsum are more mobile and are often effective in treating subsoil acidity. The effectiveness of gypsiferous materials in increasing subsoil pH is variable because the self-liming effect of gypsum occurs as a result of ligand exchange of sulfate anion for hydroxyl anion on hydrous Fe and Al surfaces [21]. Ligand exchangeable hydroxyl anions must be present on the relevant variable charge soil surfaces for self-liming to occur. Some crops such as lupins are sensitive to gypsum application, and this limits its use for this crop in Western Australia. In the absence of ligand exchange, gypsum may still provide some benefits such as overcoming calcium deficiency,

increasing the Ca/Al ratio, and increasing the ionic strength of the soil solution and hence decreasing the relative activity of Al.

The variable success of lime and gypsiferous materials in controlling subsoil acidity has led to research on the use of soluble organic materials to treat the problem. One of the first products used was calcium fulvate obtained from the wet oxidation of coal and neutralization of the water-soluble product with calcium hydroxide. In a column experiment, calcium fulvate was consistently found to increase soil pH to a depth of 100 cm after application of two pore volumes of water in soils containing 6, 20, and 36% clay, whereas application of the same amounts of calcium as gypsum decreased subsoil pH and lime (applied as calcium hydroxide or as calcium carbonate) had little effect below the depth of application [18]. The sulfate-induced self-liming effect of gypsum was not apparent in these soil samples, and the salt effect resulted in lower pH values.

Further soil column experiments using calcium fulvate and a less soluble oxidized calcium-saturated coal product again showed the inability of lime to treat the soil below the depth of incorporation, whereas the coal products were able to ameliorate acidity at depth in a red podzol by increasing soil pH and decreasing exchangeable Al [54]. Similar work on a repacked 50-cm-long column of an Ultisol (pH 4.4) showed that only 2% of added lime moved past the 15-cm depth with 300 mm leaching with water. Lime had no effect on exchangeable aluminium below 10-cm depth. In contrast, 35–75% of calcium fulvate derived from chicken manure, cowpea green manure, and sewage sludge moved beyond this depth. The calcium fulvate derived from sewage sludge decreased Al down to the 45-cm soil depth. The other calcium fulvates were less effective [55]. Calcium fulvate derived from a pasture soil and calcium citrate were also found to be effective in ameliorating the subsoil by complexing and removing Al from the soil column. Calcium chloride and phosphogypsum were unable to displace Al from the column [56]. Although these examples show the effectiveness of organic materials in ameliorating subsoil acidity and aluminum toxicity under laboratory conditions, little work has been done in assessing their potential in the field from the point of view of waste management, economics, environmental impact, and crop yield.

5 AMELIORATION OF ALUMINUM PHYTOTOXICITY BY ROOT EXUDATION OF ORGANIC MATTER

Root apices (terminal 3–5 mm of roots) are the primary site of Al-induced inhibition of root growth, and many plants have evolved resistance to Al phytotoxicity by releasing simple low-molecular-weight aliphatic organic acids at the root apex to complex soluble toxic Al. The organic acids released include citrate and malate, which react strongly with Al and convert it to less toxic organically bound forms. The organically bound Al is less readily taken up by root apices and is hence excluded from the plant. Cultivars differ considerably in their ability to detoxify Al

in this way and give rise to genetic-based variability in resistance to Al. This mechanism of Al detoxification has been reported in tolerant cultivars of many crops including barley, buckwheat, canola, lupins, maize, oats, snapbeans, soybeans, and wheat. Resistance to Al and root growth in soybean cultivars is related to the rate of root exudation of citrate, which is induced specifically by exposure to Al. Other metals and P deficiency failed to induce citrate exudation. Plants take up the Al-citrate complex poorly, and this allows root growth to increase while Al uptake decreases due to Al exclusion from the root apex [57].

Maize exudes malate in addition to citrate. When the roots of tolerant and sensitive maize plants were grown in nutrient solutions containing a series of Al concentrations, dose-dependent citrate and malate exudation was observed in the tolerant but not the sensitive roots. The rate of citrate exudation was two to four times that observed for malate [58]. Exudation of malate is more important than citrate for conferring Al resistance in wheat. Tolerant genotypes release 5 to 10 times more malate than a near-isogenic but sensitive genotype. Malic acid release is detected as quickly as 15 minutes after exposure to 200 μM Al and is stimulated with as little as 10 μM Al. The amount released increased linearly over 24 hours and was dependent on the external Al concentration. Only Al triggered the release of malic acid at root apices. Other metals and P deficiency were unable to elicit this response [59]. Other studies of wheat showed that roots of tolerant cultivars release 100–120% more malate on exposure to Al than sensitive cultivars, where exudation of malate is decreased [60]. Half-maximal efflux of malate from root apices of Al-tolerant wheat seedlings occurred at 30 M Al in 0.2 mM $CaCl_2$, pH 4.2. Maximum efflux of 2.0 nmol apex^{-1} hr^{-1} occurred with concentrations greater than 100 μM Al [61]. A study using 36 genotypes of wheat showed a significant correlation between relative tolerance to Al (estimated from the length of Al-exposed roots expressed as a percentage of the root length achieved under Al-free conditions) and the amount of malate released from root apices under standard Al treatment [62]. Plant breeding and genetic engineering offer an additional means of matching crops to Al toxic soils, but this may reveal other plant nutritional and environmental problems.

The work on Al exclusion by organic matter complexation at root apices was done in culture solutions. The strong relationship between pH and pAl in many acid soils suggests that the chelating effect of root exudation of soluble organic acids on Al activity surrounding the root tip would be transient because the pressure would be for the equilibrium Al activity to be reestablished quickly. Simple organic compounds such as malate undergo rapid microbial decomposition in soil. The half-life in soil is about 1.7 hours irrespective of the soil pH between pH 4.3 and 5.0 [63]. Decarboxylation is a major process of organic matter decomposition under aerobic conditions. It appears that malate efflux from apices of Al-tolerant wheat roots occurs as potassium malate [61]. Decarboxylation of unprotonated malate and citrate is expected to increase the pH of the rhizosphere and

provide the root tip with an additional mechanism for Al exclusion by precipitation. As root growth occurs, the anticipated loss of Al detoxification in the original zone of the root tip would not be important because the rest of the root is much less sensitive to Al toxicity. Continuous production and exudation of Al-binding organic acids are required at the root apex in order to escape the effects of Al toxicity as new soil volumes are explored.

6 NUTRITIONAL EFFECT OF ORGANIC MATTER ADDITIONS

Calcium and magnesium deficiency is common in acid soils and exacerbates the problem of Al phytotoxicity. Provision of these base cations alleviates to some extent the effect of Al toxicity on roots (64). It is suggested that the mechanism of toxicity alleviation is reduction of Al accumulation in root apices (65). The calcium and magnesium content of organic matter is expected to alleviate further the effect of Al phytotoxicity. Phosphorus (P) deficiency is also often associated with Al phytotoxicity. Plant residues and manures contain significant amounts of inorganic and organic P, and addition of organic amendments with C/P <100 alleviates P deficiency. The release of inorganic P contributes to both the soil solution and adsorbed pools. Adsorption of P derived from organic matter will decrease the sorption of a further addition of fertilizer P by occupying the more active sorption sites first. As well as direct addition of P, organic matter ameliorates P deficiency by reacting with soil and fertilizer. Organic matter addition decreases the activity of Al and Fe in soil solution by (1) increasing soil pH and (2) forming strong complexes with these metallic ions. The lowered Al and Fe activities decrease the precipitation of P with these metallic ions and decrease the amount made unavailable to plants. Low-molecular-weight aliphatic organic anions such as citrate, tartrate, and malate released into the rhizosphere by some plants have a similar effect in decreasing Al and Fe activities and increasing P availability and uptake by roots. These organic anions are also added as part of the organic residue or are formed as a result of residue decomposition. The organic Al affinities or stability constants are in the order citrate $>$ tartrate $>$ malate [7]. The functional groups involved in metal complexation are COOH and OH. These functional groups are also prevalent in humic and fulvic acids. Complexation of Al and Fe by these groups will favor the dissolution of P already precipitated with a range of Al and Fe minerals.

The concentration of P in soil solution is mainly regulated by specific adsorption–desorption reactions. Specific adsorption occurs when solution P anion replaces ligands such as OH^- ions and/or OH_2 molecules from hydrous Fe or Al surfaces to form surface complexes. The presence of large hydrous Fe and Al surface areas in highly weathered acid soils such as Oxisols and Ultisols and in volcanic soils with andic properties is the main reason for strong P adsorption and high P requirement in these soils. These surfaces have a high zero point of charge

and may be positively charged in acidic conditions. The positive charge would also retain P anion by nonspecific coulombic attraction. Increased soil pH and increased negative charge following organic matter addition decrease P adsorption by providing an unfavorable negatively charged environment for adsorption.

In some soil types, specific adsorption of P is decreased by competition for P adsorption sites by organic anions. Simple organic anions such as citrate and oxalate that are released in the rhizosphere are very effective in decreasing the specific adsorption of phosphate. Malate is moderately effective. This effect is in addition to decreasing Al and Fe activities. The effectiveness of these anions in decreasing P adsorption is determined by the relative stabilities of the Fe (or Al)–organic anion complex and the Fe (or Al)–phosphate complex. Polygalacturonate, which is a pectic substance found in mucigel surrounding root surfaces, is very effective in this regard [66]. Humic and fulvic acids compete strongly with P for adsorption sites on goethite, gibbsite, and tropical soils at acidic pH values. These acids decrease P adsorption further by generating an unfavorable negatively charge electric field around the adsorbed humic and fulvic acid molecules [67]. The effect of organic matter on P sorption appears dependent on the size of the molecule. Dissolved organic matter derived from green manure (molecular weight 710 to 850) was found to inhibit P sorption compared with DOC derived from animal manure (molecular weight 2000 to 2800), which had no effect on P sorption [68]. Addition of humic and fulvic acids does not always decrease P sorption in soils. In volcanic soils, the new humic acid–Al complex formed by adsorption of humic acid acts as a new source of P sorption sites [69]. Hue [16] showed that the efficiency of fertilizer P was improved when applied with green or animal manures. In the case of rock phosphate, mixing with animal manures, composts, or plant residues improves dissolution by removing and chelating calcium from the fertilizer (69). The added benefit of using organic matter to alleviate Al phytotoxicity is that plant nutrients are recycled and soil organic matter levels and physical and chemical conditions are improved.

7 APPLICATION IN MANAGING ACIDITY IN FARMING SYSTEMS

Addition of undecomposed plant residues, composts, and manures increases soil pH by transferring alkalinity from one place to another. The pH benefit of organic matter addition is at the expense of the place of origin of this alkalinity. Most plants using nitrate as their main source of nitrogen increase the rhizosphere pH due to excess anion uptake over cation uptake and the release of bicarbonate or hydroxyl ions to maintain electrical neutrality. These plants are poor in taking up and transferring alkalinity. Leguminous plants relying mainly on nitrogen fixation take up excess base cations over anion and release protons in the rhizosphere to maintain electrical neutrality. Similar excess cation uptake and rhizosphere acidification oc-

cur with plants fed with ammonium ions as the main source of nitrogen. The harvest and use of plant materials result in a net transfer of alkalinity from the site of rhizosphere acidification. Deep-rooted perennial leguminous plant species such as lucerne and agroforestry tree species can be used in farming systems to redistribute alkalinity from more alkaline areas to where acid amelioration is needed. The spatial distribution of the source of alkalinity varies in different landscapes. The source of alkalinity may be vertically below the acid soil layer and may occur in the form of basic saprolite or alkaline soils within the root zone of the deep-rooted plants. In other cases, the entire root zone may be acid, but spatial variation in soil pH may occur at the landscape scale as a result of pedogenic processes.

A common example that occurs on the ancient drainage landscape in Western Australia [70] is calcium carbonate accumulation in the lower parts of the landscape, whereas soils in the upper parts are acidic. Two examples of agroforestry systems in South Sumatra for the redistribution of alkalinity to deal with their different spatial distributions in the landscape have been described [71]. First, a hedgerow intercropping system with shallow-rooted crops grown between alleys of trees was used to redistribute alkalinity from lower parts of the profile to the topsoil. Second, pure stands of trees were grown and prunings cut, transported, and applied on the acid soil to demonstrate the transfer of base from the production to the mulch plots. Both systems were effective in treating soil acidity, and the system recommended takes into account the location of source of alkalinity. Prunings from the *Gmelina* tree had a high base cation content but were unsuitable for hedgerow intercropping because it outcompeted the crops [71]. This tree species should perform well in a lateral base transfer and mulch system that can also incorporate animals and the recycling of manure. Amelioration of Al toxicity is therefore only one of the terms in an overall tree–soil–crop interaction and other criteria should be assessed simultaneously.

8 CONCLUSIONS

Laboratory work has shown that the major effect of a wide range of organic materials on soil acidity is increased soil pH. There are additional benefits in lowering the solubility of soil Al so that lower activities are obtained at a given soil pH. This lowering of Al activity can also be achieved by direct Al complexation by organic acids released by root apices of Al-tolerant plant species and varieties and released by added organic materials. The pH effect of organic matter is expected to extend to the subsoil better than liming materials because of higher solubility of simple low-molecular-weight organic acids and of fulvic acids. The pH effect of organic matter additions can be predicted under laboratory conditions. Increases in pH due to ammonification are short lived because of subsequent acidification through nitrification. The effect of decarboxylation and proton flows between pH buffer systems is long lasting.

This knowledge can be used to develop farming systems that conserve and transfer alkalinity to more acid surfaces in the landscape. There is little evidence so far that an integrated approach is being taken to manage acidity in low-input farming systems to take account of possible significant fluxes of alkalinity within and from the farms. There is an urgent need to develop such an approach, which will enhance the environment by conservation and by providing a valuable use for a wide range of organic waste materials. Development of a research and demonstration village-scale model to test the sustainability of such a system under real-life conditions would be the first step toward such an integrated approach. An additional benefit of organic matter use is the recycling of plant nutrients and increased nutrient availability due to both direct addition and reactions with soils and fertilizers that increase nutrient availability, especially phosphate availability.

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13

Fertility Management of Tropical Acid Soils for Sustainable Crop Production

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1 INTRODUCTION

Tropical regions have the largest land area available for agricultural production to meet growing demand for food by the rapidly increasing world population. Tropical agriculture, however, is faced with a serious challenge of feeding about 70% of the world's inhabitants and meeting other basic necessities of life for 75 to 80% of the population of the region that depends on farming. A significant portion of the population in tropical countries suffers from malnutrition. In addition to economic issues, intensification and extension of agriculture to marginal lands have created severe ecological problems (e.g., deforestation, soil degradation, pollution of water and the natural environment, and increased greenhouse gas emissions). In these situations, adopting sound practical measures to maintain and/or improve the nutrient-supplying capacity of tropical soils is the key factor to improving and/or sustaining the long-term crop production.

There is a need to define soil fertility and crop sustainability in tropical soils before discussing the fertility management practices. Soil fertility is the quality of a soil that enables it to provide nutrients in adequate amounts and in proper balance for the growth of specified plants or crops [1]. Soil fertility is sometimes confused with soil productivity and soil quality. These terms are, however, distinct. Soil productivity is the capacity of a soil to produce a certain yield of crops or other plants with a specified system of management. In contrast, soil quality is the capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health [1].

Sustainable agriculture is the management and utilization of the agricultural ecosystem in a way that maintains its biological diversity, productivity, regeneration capacity, vitality, and ability to function so that it can fulfill, today and in the future, significant ecological, economic, and social functions at the local, national, and global level without adverse effects on the other ecosystems [2]. Tropical soils may be defined as all soils that occur in the geographic tropics, that is, in the region of the earth lying between the tropic of Cancer and the tropic of Capricorn, also known as the torrid zone [3]. There are diverse types of soils in the tropical regions. However, acidic, low-fertility soils meeting the stereotypic concept of tropical soils are mainly classified as Oxisols and Ultisols, covering about 43% of the tropics, including large areas in South America and central Africa [4].

Low natural and/or declining soil fertility is the main constraint on improving the yield of annual crops on most tropical acid soils. Sub-Saharan Africa is a region facing massive problems of food security due to decreasing per-capita food production. A team of international researchers has identified declining soil fertility as the fundamental cause of declining productivity in Africa [5].

Most of the central part of Brazil is occupied by a tropical savanna, locally known as the "cerrado," which covers about 205 million ha or 23% of the national territory. Most soils in this region are highly weathered Oxisols (46%), Ultisols (15%), and Entisols (15%), with low natural soil fertility, high aluminum saturation, and high P fixation capacity (Table 1). In addition to cerrado, there are about 30 million ha of lowlands, known locally as "varzea" in Brazil. At present, about 1.5 million ha of these lowlands are under cultivation. Generally, varzea soils have good initial soil fertility, but within 2 to 3 years of cultivation, fertility declines [6].

Farming systems need to be developed with improved soil management technology to bring these areas under successful crop production. Supply of sufficient amounts of nutrients is one of the key factors in improving crop yields and maintaining sustainable agricultural production on these lowlands. Soil fertility management for sustainable crop production represents a resource-efficient option in maintaining adequate nutrient levels. This is an important aspect in sustaining our soils and consequently the society. The objective of this chapter is to suggest appropriate management strategies for improving the nutrient satus of tropical acid soils for sustainable crop production.

TABLE 1 Selected Chemical Properties of Cerrado and Varzea Acid Soils of Brazil (0 to 20 cm Depth)

pH (H$_2$O)	Ca	Mg	Al	P	K	Cu	Zn	Fe	Mn	OM (g dm^{-3})	Base saturation (%)
	(mmol$_c$ dm^{-3})			(mg dm^{-3})							
				Cerrado[a]							
5.2	6.4	5.8	6.4	1.2	47.2	1.3	1.0	116	14	15	17
				Varzea[b]							
5.3	49	31	13	16	92	2.2	2.4	303	59	31	50

[a] The data are average values of 200 soil samples collected from six states covering cerrado region.
[b] The data are average values of 55 soil samples collected from eight states covering varzea soils.
Source: Adapted from Ref. 77.

2 MANAGEMENT STRATEGIES FOR REPLENISHING SOIL FERTILITY

The current knowledge of the soils in the tropics clearly indicates that there is considerable diversity of soils, and the immediate need is to manage this diversity in the context of sustainable agriculture. Liming and adequate rates of fertilizer application are the most effective management strategies to overcome acidity and soil fertility constraints to crop production in the highly weathered soils of the tropics. However, use of gypsum; control of soil erosion; maintenance of organic matter content; use of nutrient-efficient or toxicity-tolerant crop species or cultivars within species; adoption of appropriate crop rotation; creation of irrigation facilities; control of insects, diseases, and weeds, control of allelopathy; and favorable socioeconomic factors for the farmers are other complementary practices that can be adopted in fertility management of these soils for sustainable crop production. Therefore, an adequate soil fertility management program requires integration of numerous technological but also socioeconomic factors.

2.1 Liming

Soil acidity, either natural or developed by human activities, has serious negative effects on the sustainability of crop production in various parts of the world. The predominant constraint resulting from increasing soil acidity is a severe chemical imbalance caused by toxic levels of Al, Mn, and H ions coupled with a parallel critical deficiency in available N, P, K, Ca, Mg, Mo, and sometimes Zn. Ion toxicities and Ca deficiency are not necessarily mutually exclusive injuries. The micro- and macronutrient imblances result in impaired physiological, biochemical, and/or metabolic processes that affect crop growth detrimentally [7].
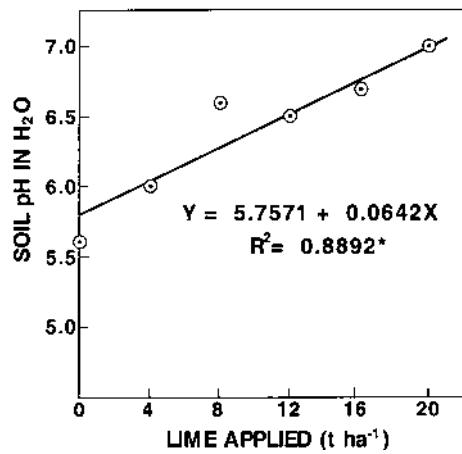
FIGURE 1 Relationship between lime applied and pH of an Oxisol of central Brazil. (Adapted from Ref. 47.)
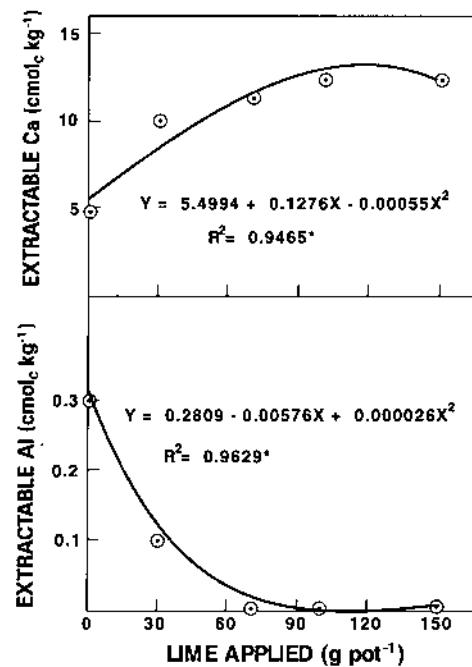
FIGURE 2 Relationship between lime applied and extractable Ca and Al concentrations in the lowland acid soil of central Brazil. (Adapted from Ref. 81.)
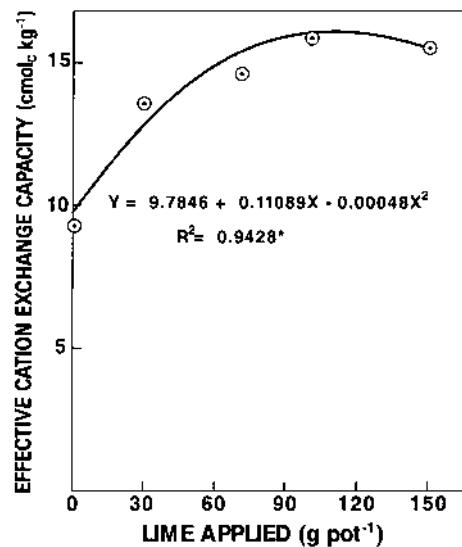
FIGURE 3 Relationship between lime applied and effective cation exchange capacity of acid lowland soil of central Brazil. (Adapted from Ref. 81.)

Improper management of agricultural systems result in the inefficient use or loss of basic cations through excessive removal in biomass and leaching losses [8,9]. Liming is the most dominant and most effective practice to replenish the soil cation pool [10]. Liming increases soil pH (Fig. 1), Ca concentration (Fig. 2), cation exchange capacity (Fig. 3), and base saturation (Fig. 4), simultaneously
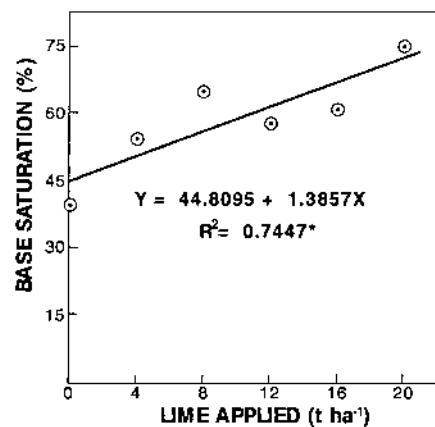
FIGURE 4 Relationship between lime applied and base saturation of an Oxisol of central Brazil. (Adapted from Ref. 47.)
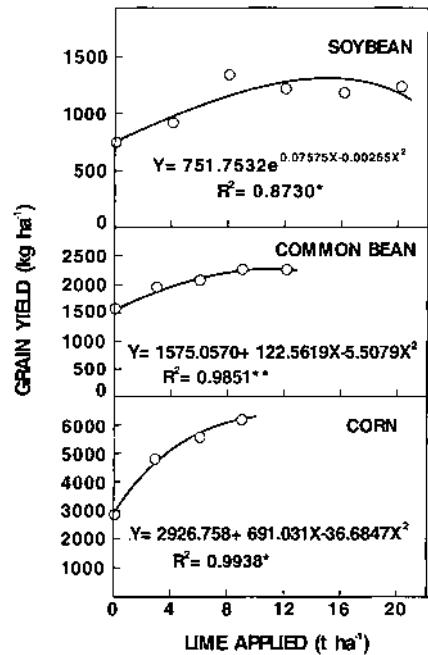
FIGURE 5 Response of soybean, common bean, and corn to liming on an Oxisol of central Brazil. (Adapted from Ref. 77.)

lowering the Al concentration (Fig. 2). All these chemical changes, provided they are within a favorable range, improve grain yields and crop sustainability. Figure 5 shows the response of soybean (*Glycine max* L. Merr.), common bean (*Phaseolus vulgaris* L.), and corn (*Zea mays* L.) to liming on an Oxisol of central Brazil. A significant quadratic response was obtained with the three crops. Based on regression equations, the maximum yield of soybean was achieved at 14 t lime ha^{-1}. In the case of common bean and corn, the maximum grain yields were obtained at 11 and 9 t lime ha^{-1}, respectively. Therefore, among these three crops soybean was most sensitive to soil acidity and corn was least sensitive. Overliming, however, may cause deficiency of some micronutrients, such as Mn, Zn, Cu, B, and Fe, if soils are relatively poor in these elements. Iron deficiency in upland rice (*Oryza sativa* L.) grown in Oxisols of Brazil has been reported [11]. The iron deficiency in these soils is caused by liming. Due to improved technologies, farmers use lime at an adequate level to raise the soil pH to about 6 and 6.5 for crops such as soybean and common bean. However, when rice is planted after these crops in rotation, it shows Fe deficiency symptoms. This deficiency is related to Fe uptake and utilization by rice plants and not to deficiency of this nutrient in the soil. Iron

in the limed soils precipitated according to following reaction:

$$Fe^{3+} + 3OH^- = Fe(OH)_3 \text{ (precipitated)}$$
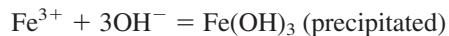
Lindsay [12] reported that an increase of one unit of soil pH above pH 4 decreases the solubility of iron by a factor of about 1000. Concentrations of other elements such as Mn, Zn, and Cu also decreased with increasing pH; however, this decrease was about 10 times lower than that of iron [12].

Base saturation, aluminum saturation, and pH are generally used as indices of soil acidity in making decisions on improving crop yields on acid soils by liming. Base saturation can be calculated by the following formula:

$$\text{Base saturation} = \frac{\sum \text{exchangeable Ca, Mg, K, Na}}{\text{CEC at pH 7 or 8.2}} \times 100$$

The pH used for cation exchange capacity (CEC) must be specified whenever the concept is to be used [13]. The base saturation philosophy is based on the principle that the maximum crop yields can be achieved by creating an ideal ratio of Ca, Mg, and K in the soil [14]. Figure 6 shows the relationship between the soil base saturation and the grain yield of common bean grown on an Oxisol of central Brazil. The maximum grain yield of this crop was achieved at 55% base saturation. Aluminum saturation is another index of soil acidity. The purpose of the aluminum saturation index is to provide a basis for lime recommendations aimed at reducing the toxic effects of Al as opposed to indices aimed at raising soil pH. The following equation illustrates the kinds of reactions that follow the addition of lime to an acid soil:

$$2Al\text{-}x + 3CaCO_3 + 6H_2O \rightleftarrows 3Ca\text{-}x + 2Al(OH)_3 + 3H_2O + 3CO_2$$
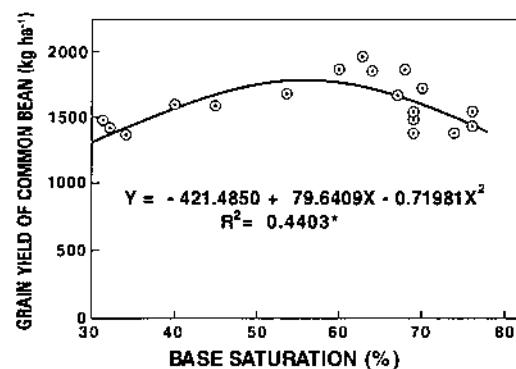
FIGURE 6 Relationship between base saturation and grain yield of common bean grown on an Oxisol of central Brazil. (Adapted from Ref. 47.)

In this equation, -x denotes an exchange site on soil solids. The reaction detoxifies aluminum by binding it to hydroxyls, causing it to become insoluble in water. Although there are many compounds that can replace Al on the exchange sites, only those that also react with hydrogen make effective liming material.

Aluminum saturation can be calculated from the following formula:

$$\text{Al saturation} = \frac{\text{Al}}{\sum \text{Ca, Mg, K, Al}} \times 100$$

Values of Al saturation can be used as an index of the lime application rate that varies from soil to soil and among crop species as well as within cultivars of the same species. Figure 7 shows the relationship between Al saturation in a lowland acid soil of Brazil and the relative grain yield of common bean. With increasing Al saturation, there was a quadratic decrease in the grain yield. The critical Al saturation values for important field crops are listed in Table 2.

Soil pH is also used as an acidity index for determining the liming rate. The optimal soil pH is the minimum pH above which liming will not increase crop yield. This is normally called the "critical" pH [15]. Figure 8 shows the relationship between the pH and the dry matter yield of wheat (*Triticum aestivum* L.), corn, soybean, lowland rice, and common bean grown on an acid lowland Inceptisol soil of Brazil. The relative dry matter yield (DMY) of shoots of all the crops tested was significantly affected by soil pH. The optimal pH for the maximum DMY of wheat was 6.3, for soybean 5.6, corn 5.4, common bean 6, and for rice 4.9. This shows that crops responded differently to soil acidity. Among the crops tested, rice was the most tolerant and wheat was the most sensitive to soil acidity.
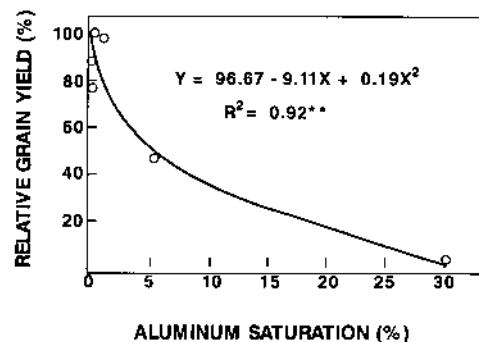
FIGURE 7 Relationship between aluminum saturation and relative grain yield of common bean grown on an acid lowland Inceptisol of central Brazil. (Adapted from Ref. 14.)

TABLE 2 Critical Al Saturation for Important Field Crops at 90 to 95% of Maximum Yield

Crop	Type of soil	Critical Al saturation (%)
Cassava	Oxisol/Ultisol	80
Upland rice	Oxisol/Ultisol	70
Cowpea	Oxisol/Ultisol	55
Cowpea	Oxisol	42
Peanut	Oxisol/Ultisol	65
Peanut	Xanthic Halpludox	54
Soybean	Oxisol	19
Soybean	Xanthic Halpludox	27
Soybean	Oxisol/Ultisol	15
Soybean	Not given	<20
Soybean	Ultisol	20 to 25
Soybean	Histosol	10
Soybean	Ultisol	20
Corn	Oxisol	19
Corn	Xanthic	27
Corn	Oxisol/Ultisol	29
Corn	Oxisol/Ultisol	25
Corn	Oxisol	28
Mungbean	Oxisol/Ultisol	15
Mungbean	Oxisol/Ultisol	5
Coffee	Oxisol/Ultisol	60
Sorghum	Oxisol/Ultisol	20
Common bean	Oxisol/Ultisol	10
Common bean	Oxisol/Ultisol	8 to 10
Common bean	Oxisol/Ultisol	23
Cotton	Not given	<10

Source: Adapted from Ref. 14.

The quantity of lime added depends on the soil type, the quality of liming material, crop species, cultivars within species, and economic considerations. In Brazil, liming recommendations are based on soil exchangeable Al, Ca, and Mg. The lime requirement (LR) is calculated using the following formula:

$$\text{LR (metric tons ha}^{-1}) = \text{Al}^{3+} \times 2 + [2 - (\text{Ca}^{2+} + \text{Mg}^{2+})]$$

The lime requirement computed from the Al, Ca, and Mg contents is based on the assumption that Al toxicity and Ca and Mg deficiencies are the most important growth-limiting factors in acid soils. In areas where lime is costly or dif-
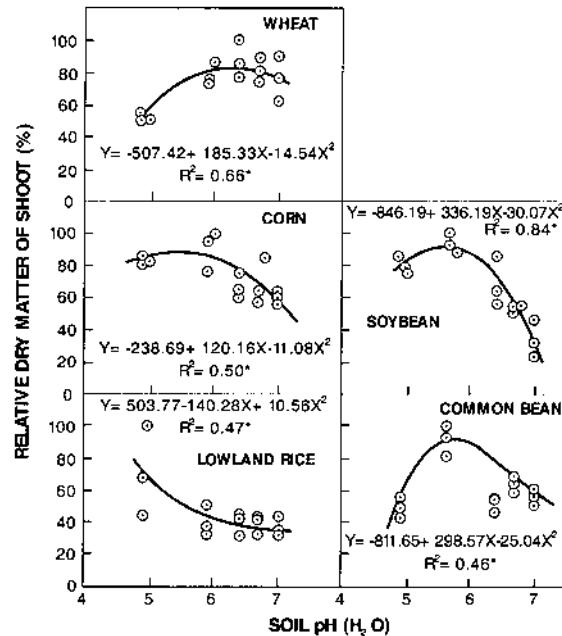
FIGURE 8   Relationship between soil pH and relative dry matter yield of five annual crops grown on an Inceptisol of Brazil. (Adapted from Ref. 81.)

ficult to obtain, it may not be practical to neutralize all of the exchangeable aluminum:

$$CaCO_3 \text{ equivalent (t ha}^{-1}) = 1.8 \, [Al - CAS(ECEC)/100]$$

where CAS is the critical aluminum saturation of the effective cation exchange capacity (ECEC). The ECEC is the sum of exchangeable Al, Ca, Mg, and K in $cmol_c$ kg^{-1} of soil in the 1 M KCl extract at the original soil pH.

In some parts of Brazil, base saturation is being used as a parameter to calculate lime requirement using the following formula:

$$LR \text{ (metric tons ha}^{-1}) = \frac{EC(B_2 - B_1)}{TRNP} \times df$$

where EC is the total exchangeable cations ($Ca^{2+} + Mg^{2+} + K^+ + H^+ + Al^{3+}$) in $cmol_c$ kg^{-1}, B_2 is the optimal base saturation, B_1 is the existing soil base saturation, TRNP is the total relative neutralizing power of liming material, and df is the soil depth factor (1.0 for 20 cm, 1.5 for 30 cm depth). For Brazilian Oxisols, the optimal base saturation for most annual crops is considered to be in the range of 50 to 60% [16].

2.2 Use of Gypsum

Gypsum ($CaSO_4 \cdot 2H_2O$) has been used to alleviate both physical and chemical growth-limiting factors for roots [17]. Radcliffe et al. [18] reported that gypsum increased the subsoil root growth, which, in turn, improved water and nutrient uptake. In some cases, base cation leaching is desirable when the depth of rooting of Al-sensitive crops is limited by high Al saturation in the subsoil. Calcium accumulation in deeper layers can reduce the effects of subsoil acidity, thus allowing deeper crop root growth to tap into subsoil water during periods of surface soil moisture deficit [19]. The amount and the degree of cation leaching in soils of the humid tropics range widely, reflecting various factors that control leaching. For example, Ca movement is promoted by applying Ca in forms that include a mobile anion, such as $CaSO_4 \cdot 2H_2O$ (gypsum) or $CaCl_2$, rather than as $CaCO_3$ (lime).

In cerrado soils of Brazil, gypsum is recommended for annual crop production on the basis of clay content using the formula [20]:

Gypsum requirement ($kg\ ha^{-1}$) = 50 × clay content (%)

In addition to Ca, gypsum can supply S to growing plants and Ca can leach to subsoil horizons where native Ca levels may be too low to support root growth. The ionic strength of the soil solution is increased by gypsum, and the increased strength lowers the activity of Al^{3+}. Furthermore, sulfate forms ion pairs with Al, such as $AlSO_4^+$, which is nontoxic to plants [21].

2.3 Use of Optimal Rate of Essential Nutrients

Three main criteria can be used in defining an adequate rate of essential nutrients. The first criterion is the soil test calibration data relating nutrient concentration and crop response. This approach is applicable to immobile nutrients in the soil–plant system. In case of mobile nutrients such as N, the soil test calibration data have little use, and crop response curves relating the N rates and the yield should be more useful in making N fertilizer recommendations. Conducting soil and plant analysis is the other approach that can be used in determining optimal rates of essential nutrients in crop production and maintaining the sustainability of agricultural systems [22].

2.4 Nitrogen Deficiency

Nitrogen deficiency is a major limitation to plant growth on acid soils in both tropical and temperate regions. In tropical America, N deficiency is a major soil constraint over 93% of the region occupied by Oxisols and Ultisols [23]. The main reasons for widespread N deficiency in these and other similar regions in the tropics are (1) a lower rate of N application than the amount removed in harvested crops or lost by other processes and (2) the decreases in organic matter content

with successive cultivation. Table 3 shows the response of rice and common bean crops to fertilization on cerrado and varzea soils of Brazil. Similarly, Table 4 shows the response of flooded rice to N application on a varzea soil. The rice crop responded significantly up to 210 kg N ha^{-1}; however, 90% of the maximum yield was obtained at about 100 kg N ha^{-1}. Brazilian farmers use only an average of 60 kg N ha^{-1} for flooded rice.

TABLE 3 Response to Fertilization of Rice and Common Bean Grown in Rotation in Cerrado and Varzea Acid Soils

Fertility level	Rice grain yield (t ha^{-1})[a]	Common bean grain yield (t ha^{-1})[1]
Cerrado soil[b]		
Low	1.7b	1.2c
Medium	2.1a	1.8b
High	2.1a	2.2a
Medium + green manure	2.4a	1.5a
F test	*	**
Varzea soil[c]		
Low	4.3b	2.9b
Medium	5.5a	6.6a
High	5.5a	8.5a
Medium + green manure	6.3a	8.2a
F test	**	**

[a] Values are averages of three crops grown in rice–bean rotation. *, **, Significant at the .05 and .01 probability levels, respectively. Within the same column, means followed by the same letter do not differ significantly at the .05 probability level by Tukey's test.

[b] Cerrado soil fertility levels for rice were low (without addition of fertilizers), medium (50 kg N ha^{-1}, 26 kg P ha^{-1}, 33 kg K ha^{-1}, 30 kg ha^{-1} fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level). *Cajanus cajan* L. was used as a green manure at the rate of 25.6 t ha^{-1} green matter. For common bean, the fertility levels were low (without addition of fertilizers), medium (35 kg N ha^{-1}, 44 kg P ha^{-1}, 42 kg K ha^{-1}, 30 kg ha^{-1} fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level).

[c] Varzea soil fertility levels for rice were low (without addition of fertilizers), medium (100 kg N ha^{-1}, 44 kg P ha^{-1}, 50 kg K ha^{-1}, 40 kg ha^{-1} fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level). *Cajanus cajan* L. was used as a green manure at the rate of 28 t ha^{-1} green matter. For common bean, the fertility levels were low (without addition of fertilizers), medium (35 kg N ha^{-1}, 52 kg P ha^{-1}, 50 kg K ha^{-1}, 40 kg fritted glass material as a source of micronutrients), and high (all the nutrients were applied at double the medium level).

Source: Adapted from Refs. 6 and 79.

TABLE 4 Response of Lowland Rice to Nitrogen Fertilization on a Lowland Acid Soil of Central Brazil

N rate (kg ha^{-1})	Response (t ha^{-1})			
	1st crop	2nd crop	3rd crop	Average
0	3.6	3.8	3.7	3.7
30	3.9	5.0	4	4.3
60	5.4	6.2	5.3	5.6
90	5.9	5.9	5.1	5.6
120	6.2	7.0	5.6	6.3
150	6.4	6.9	5.7	6.4
180	7.1	6.5	5.5	6.4
210	6.9	7.0	5.3	6.4
F test (N)	**	**	**	**
F test (Crop)				**
F test (N $\times$ Crop)				*
CV (%)	8	10	12	10
Regression				
β_0	3.40	3.90	3.56	3.62
β_1	0.03	0.04	0.03	0.03
β_2	−0.00008	−0.0001	−0.00009	−0.00009
R^2	0.96**	0.91**	0.91**	0.96**

*, **, Significant at the .05 and .01 probability levels, respectively.
Source: Adapted from Ref. 47.

Fractional application of N is an important management practice to improve N-use efficiency and improve crop yields. There was a significant difference in the grain yield when N was added in several applications during the lowland rice growth (Table 5). The addition of soluble salts of Ca, Mg, and K may also improve N fertilizer efficiency by reducing the soil solution pH. In a series of studies, Fenn et al. [24–26] found that adding soluble Ca salts to soils actually decreased NH_3 volatilization from surface urea applications and postulated that the added Ca^{2+} would precipitate with carbonate formed during urea hydrolysis, removing Ca^{2+} from the exchange complex.

Foliar application of urea has been demonstrated to be an effective method of nitrogen fertilization for cereals since the 1950s [27]. It has been suggested that there are several potential benefits of providing N to cereals via the foliage as urea solution. These include (1) reduced nitrogen losses through leaching, volatilization, and denitrification compared with N fertilizer applications to the soil; (2) the ability to provide N when root activity is impaired, e.g., in saline or dry conditions; and (3) uptake late in the season to increase grain nitrogen concentration [27].

TABLE 5 Lowland Rice Grain Yield Under Different Timing of N Application on an Acid Inceptisol of Central Brazil

Nitrogen application timing[a]	Location 1 (t ha^{-1})	Location 2 (t ha^{-1})	Average (t ha^{-1})
T1	7.1bc	7.2a	7.2ab
T2	7.8a	7.0ab	7.4a
T3	7.7a	6.9ab	7.3a
T4	7.3abc	6.8ab	7.1ab
T5	7.5ab	6.7ab	7.1ab
T6	7.3abc	7.0ab	7.2ab
T7	6.9c	6.7b	6.8b
F test (treatment)	**	*	**
CV (%)	7	8	8

[a] The 90 kg N ha^{-1} application timing was (1) total at sowing (T$_1$); (2) one-third at sowing + one-third at active tillering + one-third at panicle initiation (T$_2$); (3) one-half at sowing + one-half at active tillering (T$_3$); (4) one-half at sowing + one-half at panicle initiation (T$_4$); (5) two-thirds at sowing + one-third at active tillering (T$_5$); (6) two-thirds at sowing + one-third at panicle initiation (T$_6$); and (7) one-third at sowing + two-thirds at the start of tillering (T$_7$).
*,**, Significant at the .05 and .01 probability levels, respectively. Means in the same column followed by the same letter are not significantly different at the .05 probability level by Tukey's test. Values in the column for each location are averages of 2 years of field experimentation.
Source: Adapted from Ref. 78.

Cyanobacteria contribute to the N economy of flooded rice fields by reducing N$_2$ to NH$_3$. Several improved mutant N$_2$-fixing prokaryotes with the ability to excrete NH$_3$ have been produced, including mutants of *Klebsiella pneumoniae* [28], *Nostoc muscorum* [29], *Spirillum lipoferum* [30], and *Azotobacter* species [31]. Spiller et al. [32] produced a nitrogenase-derepressed mutant strain of the cyanobacterium *Anabaena variabilis* (strain AS-1) that is capable of excreting NH$_3$ produced by nitrogenase. Kamuru et al. [33] reported that the contribution of the mutant cyanobacterium to growth and yield of rice plants was equivalent to the application of 71 to 73 kg N ha^{-1} as (NH$_4$)$_2$SO$_4$. These authors also reported that the NH$_3$-excreting strain of *A. variabilis* shows potential for development for use as a biofertilizer in paddy rice production in areas where inorganic fertilizer N is unavailable or expensive and in rice production systems that aim to minimize environmental pollution from inorganic N fertilizers.

The nutrient budgets for sub-Saharan Africa show a net annual depletion of N, P, and K as a result of long-term cropping with little or no external nutrient input [34]. This depletion of soil nutrients is particularly high in the densely populated humid and subhumid highlands of East Africa [35,36]. Highlands (altitude

1200 to 3300 m) represent only about 20% of the total land area in East and Central Africa, but they contain about 60% of the population [37]. Although much of the highlands has a high potential for food production because of favorable seasonal precipitation, many of the soils are deficient in nutrients, particularly P [38,39]. In addition to the nutrient-depleting effects of long-term cropping, low native soil P and high fixation of P contribute to P deficiency in the highlands [40,41]. An essential ingredient for increasing crop yields in the highlands, therefore, is to increase the supply of plant-available P [39,42].

2.5 Phosphorus Deficiency

Phosphorus deficiency has generally been identified as one of the major limiting factors for crop production in highly weathered soils such as Oxisols and Ultisols in the tropics [23,43]. There is low natural P as well as low availability of P in these soils due to the reaction of soluble P with iron and aluminum oxides [11]. Phosphorus deficiency is one of the most yield-limiting factors for crop production on cerrado as well as varzea soils of Brazil [44,45]. The two main reasons for the occurrence of P deficiency in these acid soils are a low native soil P content and a high P fixation capacity. The P fixation capacity of an Oxisol from central Brazil was studied over a period of 80 days by Fageria and Barbosa Filho [46], who concluded that the amount of P fixed (i.e., not recovered by Mehlich-1 extracting solution) increased from 45 to 268 kg P ha^{-1} when the P application rate was increased from 50 to 400 kg P ha^{-1}. This means these types of soils require large amounts of fertilizer P for optimal crop production.

When extractable soil P increased, grain yield of common bean grown on an Inceptisol of central Brazil increased significantly in a quadratic fashion (Fig. 9).
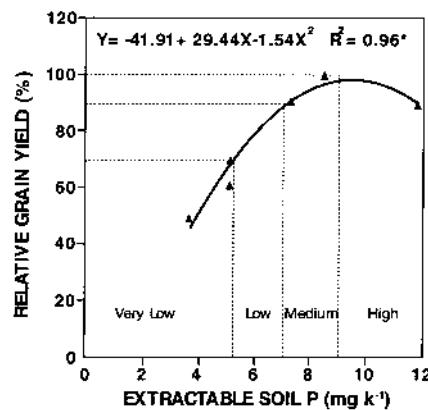
FIGURE 9 Relative grain yield response of common bean to Mehlich-1 extractable soil P in an acid Inceptisol of central Brazil. (Adapted from Ref. 80.)

TABLE 6 Mehlich-1 Soil Test P Availability Indices and P Fertilizer Recommendations for Common Bean Grown on an Acid Inceptisol of Central Brazil

Soil P test (mg kg^{-1})	P test interpretation	Relative yield (%)	Broadcast P application (kg ha^{-1})[a]	Band P application for maximum yield (kg ha^{-1})[b]
0–5.3	Very low	0–70	153	66
5.3–7.1	Low	70–95	245	44
7.1–9.0	Medium	95–100	332	44
>9.0	High	100	>332	22

[a] Rate required to achieve the soil P test category shown, not the rate for maximum yield at the given soil test category.
[b] Additional banding P rate required for maximum yield following broadcast fertilization with P to reach the soil test P level.
Source: Adapted from Ref. 80.

Similarly, Fageria et al. [45] reported a significant increase in grain yield of lowland rice with increasing P levels in these soils. Four categories were established for the P soil test: very low (VL), low (L), medium (M), and high (H) in relation to grain yield response zones (where VL = 0 to 70% relative grain yield, L = 70 to 95%, M = 95 to 100%, and H = 100%). The sufficiency P level is generally defined as 90 to 95% relative yield and coincides with the low limit of the medium or optimal range. This is the standard convention for soil test calibration research. The soil P test availability indices and P fertilizer recommendations for common bean are presented in Table 6. Fageria et al. [45] also presented soil P test availability indices and P fertilizer recommendations for lowland rice grown on a Brazilian Inceptisol.

2.6 Potassium Deficiency

The responses of annual crops to K fertilization are not as widespread and not as significant as the responses to N and P fertilization in cerrado and varzea soils of Brazil. Potassium, however, is absorbed in large quantities by annual crops, especially by high-yielding cultivars. A single upland rice crop grown on an Oxisol of cerrado soil producing 4.8 t ha^{-1} of grains in about 130 days took up 159 kg N ha^{-1}, 13 kg P ha^{-1}, and 189 kg K ha^{-1} [47]. This means that in situations where intensive agriculture is practiced, failure to replace K that is removed in harvested crop can result in K deficiency becoming a limitation to further crop production. Large positive responses of upland and lowland rice to K fertilization in cerrado and varzea soils of Brazil have been reported by Fageria et al. [48,49]. Three management practices can be used to improve K fertilizer use efficiency by plants

growing on acid soils. First, K fertilizers should be applied at an economically feasible rate, bearing in mind the need, in the long term, to replace K lost through crop removal and leaching. Second, the incorporation of crop residues in the soil after harvest enables a substantial amount of the plant K to be recycled. Approximately 85 to 92% of the total K content remains in the shoot of cereals such as rice and corn and 54 to 65% remains in the shoot of legumes such as common bean and soybean [50]. The third practice involves the use of K-efficient cultivars that have increased K uptake efficiency [11].

2.7 Calcium, Magnesium, and Sulfur Deficiency

Deficiencies of Ca and Mg are important limitations to plant growth in acid soils. Depending on the yield and the particular crop, about 26 to 53 kg Ca ha^{-1} and 12 to 26 kg Mg ha^{-1} can be removed from an Oxisol of central Brazil [47]. Crop requirements of Ca and Mg in deficient soils can be fullfilled with the application of dolomitic lime and gypsum. The lime rates applied on Brazilian acid soils can increase exchangeable Ca significantly (Table 7). When corn was grown on this soil, liming increased the grain yield significantly. At 8 t ha^{-1} lime rate, the grain yield was 31% higher compared with control treatment. Adequate Ca and Mg levels as well as Ca and Mg were also determined for upland rice, common bean, corn, and soybean grown in sequence on a Brazilian Oxisol (Table 8), showing a variation from crop species to species. Upland rice was most tolerant to soil acidity and soybean was most sensitive. In some Brazilian cerrado soils with sulfate-S below 10 mg kg^{-1}, crop responses to applied S have been reported [51]. In these

TABLE 7 Influence of Lime Rate on Exchangeable Calcium and Grain Yield of Corn on a Brazilian Oxisol

Lime rate (t ha^{-1})	Ca ($mmol_c$ dm^{-3})	Grain yield (t ha^{-1})
0	19	6.5
4	23	7.7
8	30	8.5
12	31	7.9
16	33	7.7
20	38	8.2
Regression		
β_0	18.74	6.71
β_1	0.47	0.22
β_2		−0.008
R^2	0.52**	0.48**

** Significant at the .01 probability level.

TABLE 8 Relationship Between Exchangeable Ca and Mg Parameters (X) and Grain Yield (Y) of Upland Rice, Common Bean, Corn, and Soybean Grown on an Oxisol of Central Brazil

Ca and Mg parameters	Regression equation	R^2	Adequate level[a]
	Upland rice		
Ca ($mmol_c$ dm^{-3})	$Y = 4029 + 43.1X - 0.84X^2$	0.20^{NS}	19
Mg ($mmol_c$ dm^{-3})	$Y = -2800 + 12.5X - 0.52X^2$	0.81^{**}	12
Ca saturation (%)	$Y = 4071 + 31.4X - 0.48X^2$	0.22^{NS}	21
Mg saturation (%)	$Y = -595 + 696.3X - 23.3X^2$	0.70^{**}	15
	Common bean		
Ca ($mmol_c$ dm^{-3})	$Y = -1648 + 237.4X - 4.13X^2$	0.80^{**}	29
Mg ($mmol_c$ dm^{-3})	$Y = -16209 + 2844X + 113X^2$	0.43^*	13
Ca saturation (%)	$Y = -1266 + 165X - 2.2X^2$	0.62^{**}	37
Mg saturation (%)	$Y = -978 + 1429X - 44.4X^2$	0.40^*	16
	Corn		
Ca ($mmol_c$ dm^{-3})	$Y = -139 + 497X - 7.5X^2$	0.73^{**}	33
Mg ($mmol_c$ dm^{-3})	$Y = -30640 + 5708X - 209X^2$	0.81^{**}	14
Ca saturation (%)	$Y = 761 + 343X - 4.0X^2$	0.72^{**}	43
Mg saturation (%)	$Y = -17743 + 2930X - 82.5X^2$	0.81^{**}	18
	Soybean		
Ca ($mmol_c$ dm^{-3})	$Y = -131 + 81.7X - 1.03X^2$	0.96^{**}	40
Mg ($mmol_c$ dm^{-3})	$Y = -7735 + 1297X - 46.6X^2$	0.99^{**}	14
Ca saturation (%)	$Y = -1.20 + 57.9X - 0.56X^2$	0.96^{**}	52
Mg saturation (%)	$Y = -4782 + 693X - 19.2X^2$	0.99^{**}	18

[a] Adequate level was calculated by regression equation where R^2 was significant. When R^2 was nonsignificant, original soil value was considered adequate.
*, ** Significant at the .05 and .01 probability levels, respectively.

cases, crops were likely to benefit from the addition of S-containing fertilizers at the rates of 20 kg S ha^{-1}.

2.8 Micronutrient Deficiency

Micronutrient deficiencies in field crops have increased markedly because of intensive cropping systems, loss of topsoil layers by erosion, losses through leaching, liming of acid soils, a decreasing proportion of farmyard manure compared with chemical fertilizers, the increasing purity of chemical fertilizers, and use of marginal lands for crop production. The deficiency problem is also exacerbated by the high demand of modern crop cultivars for micronutrients. Relatively little research under field conditions has been conducted on micronutrient nutrition of field crops as compared with macronutrients.

Brazilian Oxisols and Ultisols are generally low in available Zn and B, and deficiency of these nutrients has been reported in upland and lowland rice, common bean, soybean, corn, and wheat [14,52]. This deficiency is due to low natural levels of Zn and B in these soils as well as worsening of the deficiency by liming. With increasing pH due to liming, the ionic forms of the micronutrient cations are converted to insoluble hydroxide or oxide compounds. In such a case, deficiency of micronutrients is expected. One typical example of this type is iron deficiency in Brazilian Oxisols in upland rice when soil pH is raised to around 6 [47]. The best management strategies are to avoid overliming these soils, maintaining the pH in the range 5.5 to 5.8. An aplication of about 2 to 5 kg Zn ha^{-1} as Zn sulfate can correct Zn deficiency in most annual crops. Foliar spray of micronutrients is also an important strategy to correct micronutrient deficiency in annual crops [27,53].

2.9 Use of Farmyard Manures

Farmyard manure may be a complementary source of N, P, and K when applied at rates based on the composition of the manure and the nutrient-supplying potential of the soil [54,55] for crops grown on tropical soils for sustainable crop production. Opportunities for resource-poor farmers in the tropical regions to increase the application of high-quality manure may be limited, particularly in the absence of large numbers of improved breeds of livestock. However, a study conducted by Jama et al. [39] suggested that limited supplies of manure could be effectively integrated with commercial fertilizers, such as triple superphosphate and urea. Net benefits for integrated use of manure with triple superphosphate and urea remained positive and comparable to those for application of all the P and N as triple superphosphate and urea. Integration of manure with inorganic fertilizers may result in the benefits of greater residual effects of organic than inorganic sources and other advantages of manure in addition to a supply of P and N (e.g., improved soil physical properties and supply of basic cations) [56].

Crop nutrient imbalance and soil and water pollution can occur when the manure application rates are greater than the crop demand [57]. Manure application may also affect weed population dynamics. Pleasant and Schlater [58] reported that 1 kg of cow manure can contain up to 42 apparently viable seeds of lambsquarters (*Chenopodium album* L). After reviewing the relevant literature, Zimdahl [59] concluded that about 20% of the seeds of certain weed species are still viable after passage through cattle (*Bos* sp.), manure storage, and application.

2.10 Maintenance of Soil Organic Matter

Soil organic matter is not just the reservoir of nutrients and water but also improves soil structure, enhances activities of beneficial miroorganisms, reduces elemental toxicity, and makes soil less susceptible to erosion. Therefore, improving and/or maintaining soil organic matter is one of the most important management

practices for maintaining fertility of tropical soils for sustainable crop production. Normally, the soil organic matter content of tropical soils decreases with cultivation. This decrease can be attributed to tillage and related soil erosion and oxidation [11]. Such a decline has emphasized the need for development of cropping systems and cultural practices that reduce soil erosion and increase soil organic matter. In humid regions where plant available water is sufficient for annual crop production, forage legumes are often used in the rotation to improve soil productivity through increased organic matter production and N_2 fixation. The practice of growing plants (such as legumes) to enhance soil productivity during the fallow period is called green fallow [60]. The benefit of legumes is attributed predominantly to increased N supply and enhanced soil quality [61].

Increased inputs of plant residues may improve the organic matter content of the soil, thus enhancing N conservation and improving soil structure. In addition, through incorporation of large amounts of organic C into soil, microorganisms may minimize residual NO_3^--N leaching from fertilizer application through immobilization of inorganic soil N [62]. The residue of high-yielding corn may account for as much as 5 to 10 t of dry matter ha^{-1}, with a C/N ratio of 40:1 to 60:1 [62]. This high C/N ratio provides a favorable condition for immobilization of N by microorganisms. The presence of ample C substrate can also cause rapid O_2 consumption, indirectly enhancing the potential for denitrification [63].

The major agent in organic matter destruction by crop production is tillage. Extensive soil tillage, which inverts or mixes the soil, introduces large amounts of oxygen into the soil and stimulates aerobic microorganisms to consume the organic matter as a food source. Use of no-till systems can reduce the rate of organic matter loss but cannot stop it completely. Crop rotations that involve long periods of sod, pasture, or hay crops usually increase soil organic matter content during these periods and thus influence subsequent crops beneficially and probably contribute to the positive rotation effect [64].

2.11 Improving Association with Mycorrhizal Fungi

The mycorrhizal relationship is thought to be important in nutrient and water uptake by plants. In tropical acid soils, a low level of P is a significant factor limiting plant growth. Just as bacteria are important for providing N to legumes through N_2 fixation, the proper selection of plants to maximize biological associations with beneficial arbuscular mycorrhizal fungi may be important for maintaining plant productivity in soils with low available P [65]. Mycorrhizal dependence [calculated as (the shoot dry weight of nonmycorrhizal / shoot dry weight of mycorrhizal plants) $\times$ 100%] quantifies the responsiveness to arbuscular mycorrhizal fungi [66]. Plant species as well as cultivars within species differ in their mycorrhizal dependence [67–70]. For example, soybean was more responsive to mycorrhiza than corn, but considerable variation occurred among soybean cultivars [69].

2.12 Exploring Plant Genetic Variability

Search for, and exploitation of, crops that are able to utilize poorly available nutrients is one strategy to improve sustainability of agriculture on marginal lands [71]. Use of nutrient-efficient or tolerant crop species and/or cultivars can be a complementary solution for crop production on low-fertility or acidic soils. Differences among crop cultivars in the efficiency of use of N, P, and K have been reported [14,50,72,73] under Brazilian conditions. Similarly, Table 2 shows differences in Al tolerance of different crop species expressed on the basis of Al saturation, with cassava, upland rice, cowpea, and peanut being most tolerant to Al toxicity and cotton, common bean, soybean, and mungbean being most sensitive.

Morphological characters such as root length, surface area, fineness (radius), and frequency of root hairs are considered to influence strongly P uptake [74]. Breeding programs aimed at developing genotypes with improved root morphology and increased contact area of root surface with soil are, therefore, considered vital in screening for P-efficient plants [75].

2.13 Other Cultural Practices

In addition to practices already discussed, nutrient uptake efficiencies of crops in tropical soils can be improved by adopting appropriate crop rotation, controlling soil erosion, using grass–legume bicultures, and controlling diseases, insects, weeds, and allelopathy. Detailed discussion of these practices under tropical conditions is given by Fageria and Gheyi [11], Fageria and Baligar [76], Fageria and Santana [77], and Fageria and Prabhu [78].

3 FAVORABLE SOCIOECONOMIC FACTORS FOR FARMERS

Favorable socioeconomic conditions (such as availability of agricultural credit at lower interest rates, reasonable price of agricultural produce, availability of fertilizers and other agricultural inputs in time, adequate transport and storage facilities, and availability of effective extension services) are some of the important factors that may govern the use of appropriate crop production technologies. If these factors are favorable, farmers are likely to use adequate production practice, which may result in a higher crop yield and a higher use of nutrients. These factors have a significant impact in adoption of appropriate technologies by farmers, particularly in developing countries [76].

4 CONCLUSIONS

The world population is expected to be about 8.5 billion in the year 2025 and more than 10 billion by the year 2050 [11]. Most of this population increase will be in the developing tropical regions. Food production in these areas needs to be in-
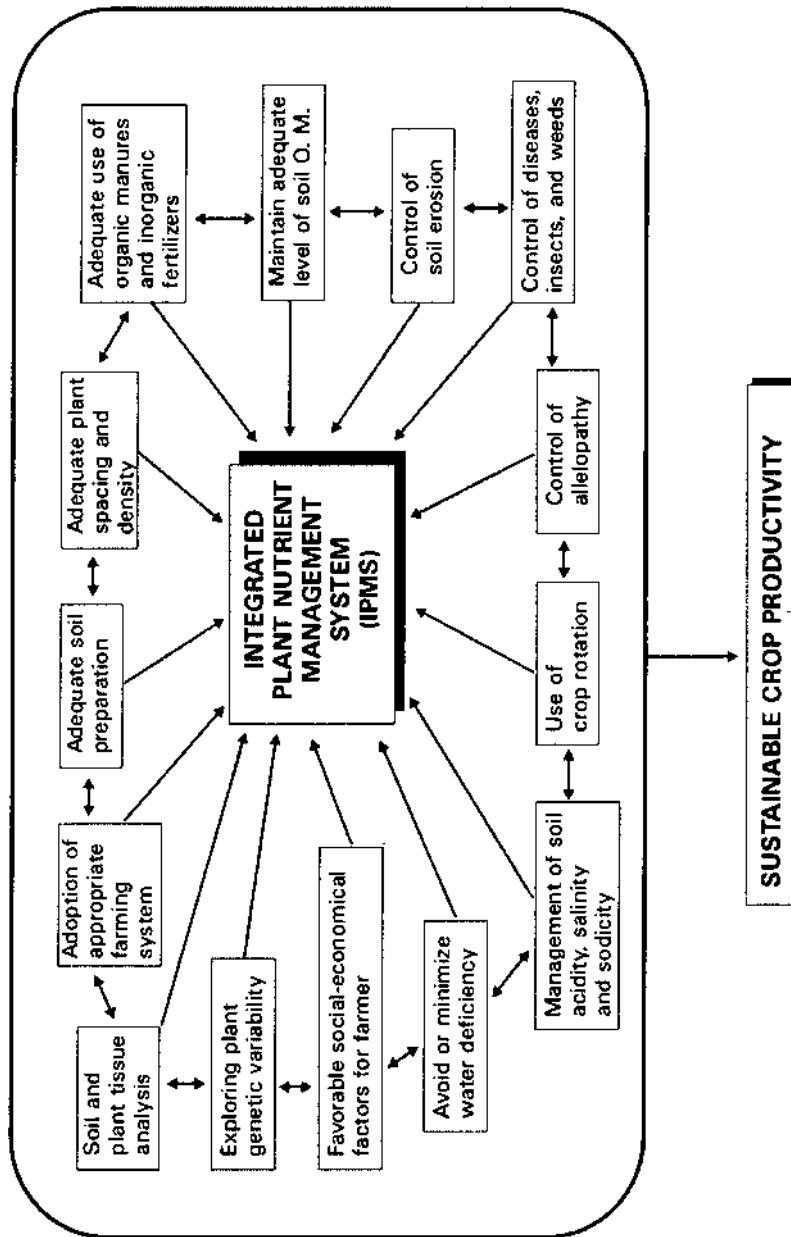
Figure 10 Integrated plant nutrient management system for sustainable crop production. (Adapted from Ref. 76.)

creased significantly to avoid hunger and malnutrition and social disorder. Therefore, the production per unit area needs to increase, and new areas have to be brought under cultivation. Because of a relatively low yield and a sufficient land area available in the tropics, there is a large potential to increase world food production. Tropical soils represent one of the largest reserves of the agricultural lands of the world that can be brought under agricultural production. These lands are an important natural resource in the biosphere, but they need to be managed with great care.

Acid, low-fertility soils in tropics (mainly classified as Oxisols and Utisols) cover 43% of the area. Improving the fertility of these soils is the first prerequisite to bringing them under cultivation for sustainable crop production. Important strategies are liming; use of adequate fertilizer rates at appropriate times during crop growth; maintenance of adequate soil moisture; conservation tillage; maintaince of soil organic matter content; reducing infestation of insects, diseases, and weeds; crop rotation; and planting nutrient-efficient and acidity-tolerant crop species and cultivars within species. Control of allelopathy and favorable socialeconomic factors for farmers are important management strategies for improving the fertility of these soils. An integrated nutrient management system should be adopted in improving the nutrient use efficiency of annual crops (Figure 10).

To put these management strategies into practice, it is necessary to use research data to provide technological packages to the farmers that may vary according to different agroecological regions as well as social and economic conditions of the farmers. Therefore, to achieve meaningful results, there is a need for synergy between research and extension, with financial support from the government as well as private agrobusiness.

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14

Role of the Genotype in Tolerance to Acidity and Aluminum Toxicity

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1 INTRODUCTION

The agronomic challenges associated with acid soils have brought plant breeders into a research arena often considered a principal concern of soil fertility and plant nutrition specialists. Their approaches, while quite different, have the same intent: to bring actual crop yields closer to potential yields by modifying the plant genotype or the soil environment. Soil acidification places productivity of currently cultivated lands at risk. As cultivation continues, the likelihood increases that nutrient toxicities and deficiencies associated with low pH will erode yield potential. Nowhere is this more apparent than in the surface-acidified areas of the U.S. southern Great Plains, site of some of the world's most intensive wheat (*Triticum aestivum* L.) production. As in other wheat-growing areas, such as Australia and South Africa, natural soil acidification is accelerated by removal of basic cations through the harvesting of vegetation and grain. Even during a period of the most intensive liming application in the U.S. Great Plains, the proportion of wheat fields with strongly acidic pH has actually increased, while those with neutral or

alkaline pH has decreased [1]. Apparently, continuous wheat production has increased soil acidification faster than the addition of lime has diminished it.

In this chapter, we intend to showcase one of nature's gifts—genetic variability—as one of the many resources available for reducing crop losses with soil acidity. We present our case not to argue genetic modification as an alternative to lime application or other soil-ameliorative approaches but as a necessary partner to them. Our discussion will center on aluminum (Al) tolerance as the central component of acid soil tolerance, not to exclude other legitimate trait systems that might be targeted in plant breeding programs, such as P utilization efficiency and Mn tolerance. Plant breeders have traditionally emphasized Al tolerance because it often evolves in plant materials common to acid soil environments.

2   SOIL ACIDITY AND GENETIC REMEDY

Two genetic forces generally provide the foundation for most crop improvement programs: extension of yield potential (assuming yield is the economic target) and reduction of susceptibility to biotic and abiotic stresses. Keeping these forces in balance is critical. Let one outweigh the other, and progress will suffer, if not cease. Improving yield via plant breeding can be compared with lifting a heavy paper sack full of groceries. The groceries inside the sack may symbolize the total yield variability or distribution from which the breeder selects. At the top of the sack is potential yield, or that which is expressed in the absence of stress, and at the bottom is yield resulting from tolerance to stress. Breeders can, and certainly do, improve yield by lifting the sack from the top—the more tempting approach and perhaps most convenient—or they may improve yield by lifting from the bottom, which tediously requires both hands but provides more stable support. One can only go so far before the sack tears if it is lifted solely from the top, i.e., if genetic progress depends solely on selection for yield potential. This analogy is especially fitting for breeding programs that target production zones limited by soil acidity. Yield *potential* means nothing when the plant is not properly equipped with a genetic mechanism that confers tolerance to critically acid soils.

Wheat cultivars currently grown throughout the Great Plains often yield in excess of 5 to 7 t ha^{-1} under optimal pH, but the same cultivars may yield nothing on acid soils in neighboring fields with critical soil acidity. As an example, we show in Table 1 the grain yield of the most popular bread wheat cultivars grown in the southern Great Plains today when measured under irrigation in the western High Plains area (near Guymon, Oklahoma, pH 7.1, minimal abiotic stress) versus under dryland conditions near Enid, Oklahoma, where low soil pH (pH 4.1, Al saturation >30%) is the predominant yield-suppressing factor. Yield potential, as approximated at Guymon, is independent of yield performance under soil acidity. Custer, the second leading cultivar currently planted in Oklahoma, has extremely high yield potential but lacks the required tolerance to low pH to be planted in al-

TABLE 1 Grain Yield of Seven Bread Wheat Cultivars in Two Great Plains Environments Contrasting for Soil Acidity—One a Richfield Clay Loam Site (pH_{H_2O} = 7.1) near Goodwell, Oklahoma and the Other a Pond Creek Silt Loam (pH_{H_2O} = 4.1) near Enid, Oklahoma—Measured in Two Crop Years (1999, 2000)[a]

Cultivar	Nonacidic (kg ha^{-1})	Acidic (kg ha^{-1})
Custer	5920	1550
Chisholm	5240	2050
2174	4850	2400
Tomahawk	4740	890
Oro Blanco	4680	2320
Jagger	4620	3100
2137	4620	2790
LSD (0.05)	810	400

[a] Expected yield in the absence of acid soil stress at Enid would be approximately 3300 kg ha^{-1}.

most 20% of Oklahoma's wheat acreage. Tolerant and sensitive cultivars may differ by as much as 3 t ha^{-1} under the acidic conditions described here, yet, as this chapter will show, their genotypic differences may be limited to a few loci relative to Al tolerance. Rarely do breeders have the capacity to manipulate a small number of genes with such enormous impact on traits of economic importance.

Genetic improvement of tolerance to soil acidity has taken on high priority in breeding programs for several major field crops grown in the United States, including alfalfa, *Medicago sativa* L. (Bouton et al., http://genes.alfalfa.ksu.edu/TAG/TAGpapers/Bouton/BoutonAlPaper.htm, March 29, 2000); soybean, *Glycine max* (L.) Merr. [2]; and winter wheat, *Triticum aestivum* L. [3]. Breeding programs have long been established in other countries for improving acid soil tolerance of maize [4] and spring wheat [5]. We searched the Current Research Information System (CRIS) to locate other USDA-CSREES and USDA-ARS–supported research programs that specifically identify acid soil tolerance as a breeding objective. Those identified include the hard winter wheat breeding program at Kansas State University (directed by A. Fritz); the cereal breeding program at University of Georgia, Griffin (directed by J.W. Johnson); and the winter wheat and ryegrass breeding programs at Texas A&M University, Overton (formerly directed by L.R. Nelson).

Genetic remediation offers several benefits complementary to, or independent of, soil amelioration. Genetic tolerance may be the most practical and economic approach in cases where tenants with short-term leases do not wish to com-

mit to long-term investment of one or more liming applications. Tolerance may also provide immediate results in crop performance that may not be realized immediately following lime application, depending on the degree of its incorporation, activation, and movement to subsurface regions. Genetic tolerance provides protection throughout the acidified zone, not only the zone of amelioration. Thus, an effective strategy might be to use acid soil–tolerant cultivars with surface lime application [6,7]. Excessive liming, or restoration of soil pH beyond the recommended level, may cause undesirable shifts in soil pathogen populations, thereby causing higher disease pressure. This yield reversal has been observed in wheat in association with take-all disease, caused by *Gaeumannomyces graminis* var. *tritici* Walker, and possibly in combination with other soilborne pathogens [8,9]. For this reason, the true response to liming has often been difficult to quantify for wheat grain yield in the southern Great Plains. Krenzer and Westerman [10] first reported only a slight increase in grain yield between nonlimed plots (pH 4.6) and plots that received 25% of the soil buffer index recommendation value. Plots receiving twice the rate actually declined in grain yield compared with the nonlimed plots. After their results were reported, infection by *Rhizoctonia cerealis,* the causal organism for sharp eye-spot disease, was found to be more severe in the limed plot areas (E.G. Krenzer, personal communication, 2000). Soil pH is not believed to have a direct effect on the root rot pathogen but may alter the soil microflora to allow the pathogen to flourish (L.R. Singleton and R.M. Hunger, personal communication, 2000). Because no effective level of resistance has yet been found in winter wheat for take-all and other root rot diseases, the adoption of acid soil–tolerant genotypes becomes even more important in managing acid soils that may harbor root rot pathogens. Finally, although any soil amendment may be effective in mitigating the effect of low pH, its coverage may not be spatially uniform across the area of production.

These scenarios point to varietal selection as a management tool, or a form of "insurance," for managing acid soils. Survey data for cultivars under cultivation in the southern Great Plains bear witness to the importance of acid soil tolerance in varietal choices made by farmers. Since 1994, the leading wheat cultivars based on acreage seeded in Oklahoma have consistently and noncoincidentally featured a high degree of Al tolerance [1].

Genetic variation for tolerance to acid soils and its chemical components have been demonstrated in a plethora of cultivated and pasture crops, thanks largely to the work of USDA-ARS scientists Dr. Charles Foy and Dr. V.C. Baligar. Foy [11] cited and summarized the research on genotypic ranges of tolerance in several plant species. Davidson [12] also summarized differences in Al and Mn toxicity tolerance for several crop and pasture species. One must interpret interspecific comparisons with caution, however, because they can be greatly skewed by wide intraspecific variability and limited intraspecific sampling of genotypes used in the bioassay. For the same reason, phytotoxicity for a range of soils is not

well predicted by the genotype(s) of a species sampled to make the prediction [13]. One message is clear from the extensive database created on genetic divergence for acid soil tolerance: the levels of genetic diversity are conducive to crop improvement via traditional hybridization and phenotypic selection of unique gene combinations. Recent advances in molecular genetics will make manipulation of the plant genotype an even more effective approach to alleviating soil acidity.

3 VARIABILITY FOR ALUMINUM TOLERANCE AND ITS GENETIC BASIS: THE CASE OF WHEAT

Genetic variation allows different plant species, and different cultivars of the same species, to exhibit differing abilities to grow in acid soils. The discovery of genetic variation for Al tolerance in wheat dates back nearly 100 years, when it had a prominent role in the earliest breeding efforts in Brazil and was instrumental to the expansion of wheat production in that country. A historical view of these breeding efforts, found in publications by Da Silva [14] and Beckmann [15], is briefly summarized here because of their relevance to later discussions of the genetics of Al tolerance in this crop.

In the early 1900s, wheat breeding efforts were initiated in areas of southern Brazil that suffered from severe soil acidity and Al toxicity. Significant variation among different wheat cultivars for a trait referred to as "crestamento," which roughly translates in English to "partially burned," was well known. At that time, the basis for crestamento was not known, although we now know it is a symptom elicited by toxic levels of Al in the soil. These effects were so great in some of these areas that selection against wheat cultivars sensitive to Al was generally 100%, with the plants dying before yielding any grain. However, a range of tolerance to crestamento in wheat was reported to exist among the cultivars that were being evaluated at the time.

Because of the strong association between tolerance to crestamento and superior performance, Al tolerance was, by default, probably the earliest trait selected for by the southern Brazilian wheat breeding programs, dating as far back as the early 1920s. One particular cultivar, Polyssu (named after the person who had identified the cultivar in a wheat field in 1914), exhibited exceptional resistance to crestamento compared with other cultivars and was used in many early crosses to other wheat cultivars. In particular, Polyssu was crossed to a series of desirable lines from earlier breeding work, referred to collectively as "Alfredo Chaves" (AC) lines. The AC lines were named after the experiment station at which they were developed and presumably also possessed superior Al tolerance to be so productive on these soils. These Polyssu $\times$ AC crosses proved to be extremely important for Brazilian wheat production; most of the important Brazilian wheat cultivars arising over the next several decades (e.g., Frontana, Colonias,

Frontiera, Rio Negro, Maringa, Toropi, BH1146) could trace their parentage back to these crosses [16]. This shared lineage among historically important Brazilian cultivars reflects a uniquely high level of Al tolerance found in Polyssu or the AC lines. The importance of the Polyssu × AC crosses is not restricted to Brazilian agriculture. Indeed, as wheat-breeding efforts on acid soils expanded globally, Brazilian wheats derived from these crosses became a cornerstone source for genes that confer Al tolerance. Thus, the production of wheat on acid soils around the world has benefited greatly from the early discoveries and research of Brazilian wheat breeders.

As Al tolerance became more recognized as a trait of importance to wheat breeding in many regions of the world, efforts were made to explore existing variation for this trait. In particular, there was a flurry of research on this topic in the 1960s and 1970s, and interest persists to this day, as future agricultural expansion is likely to be on acidic soils because of their worldwide prevalence [17]. A general outcome of all of these studies is that Al tolerance variation, when measured as a metric character such as root growth, plant weight, or yield, cannot be defined on the basis of discrete genotypic classes but rather appears to be continuous [3,18–20]. Some authors have identified generic classes of Al tolerance, such as tolerant, intermediate, or sensitive, or with more classes [16,21–25], but these are classifications of convenience and have been based on ranges of values rather than clear discontinuities or thresholds that differentiate between the classes. One of the widely used bioassays for Al tolerance in cereals, the hematoxylin root staining assay, encourages discrete classification with its visual scale of assessment. Although it serves to predict gross differences in Al tolerance, the correlation of staining score with metric classifications that directly estimate Al tolerance is far from perfect [26], particularly when Al tolerance is measured under field conditions [27].

A number of interesting findings have emerged from studies of Al tolerance variation in wheat. For instance, several studies have revealed that variation for Al tolerance among wheat cultivars is correlated with their origin [19,28,29]. Cultivars from Brazil appear to be nearly uniformly Al tolerant and to possess the greatest degree of Al tolerance, and southeastern U.S. cultivars have also exhibited significant Al tolerance. Low levels of Al tolerance have been found in cultivars developed in the western United States and the Great Plains, although the trend in the Great Plains has recently reversed with more conscious selection for acid soil tolerance. Thus, historically, a ubiquitous feature of wheat improvement efforts on acidic soils appears to have been an unconscious selection for Al tolerance, with the degree of selection reflective of the severity of the Al toxicity in the region. In contrast, in the absence of Al toxicity, selection during wheat breeding has been based on other traits whose relative impact on phenotypic variation for performance may have been reduced in acid soils due to the large effect imposed by Al toxicity. Because Al tolerance is presumed to have a neutral effect in the absence of Al toxicity (see later), there is no reason for Al tolerance to persist in new germ

plasm developed from Al-tolerant cultivars on noncritically acid soils, unless by chance or due to linkage to other desirable traits.

Another fact emerging from studies of Al tolerance variation in wheat is that Al tolerance is not an inherent characteristic of wheat but rather represents a derived state. This can be inferred from the simple observation that wheat as a rule is not particularly Al tolerant and that Al tolerance is more the exception than the rule. Further, studies of wild wheat [19,30] and durum (*T. turgidum* L. *durum*) wheat [31] have been unsuccessful in finding levels of Al tolerance approaching those found in bread wheat. Taken together, these observations suggest that hybridization events that occurred between the diploid progenitors of wheat were not between Al-tolerant landraces and that the rather restricted occurrence of extreme Al tolerance that exists in wheat today is due to mutations that accrued after the hexaploid genome of wheat was assembled through interspecific hybridization. Perhaps Al tolerance existed in the early hexaploid wheats but was selected against in early neutral-pH wheat production environments because of the metabolic cost of the trait. However, our current understanding of the physiology of Al tolerance in wheat indicates that the only definitive mechanism of Al tolerance in wheat is the exudation of malate from the terminal few millimeters of the root apex, specifically in response to Al exposure [32], suggesting that Al tolerance is remarkably conservative relative to metabolic cost. Thus, the Al tolerance trait is unlikely to have a deleterious cost to crop performance in neutral soils that would render it subject to negative selection. This hypothesis is supported by results of field studies that do not show any trend toward poor performance of Al-tolerant cultivars in the absence of Al toxicity [27,33].

To date, the various wild and domesticated species of wheat have been the focus of more Al tolerance genetic studies than any other species. The ability to trace the ancestry of the more extreme levels of Al tolerance in many Brazilian wheat cultivars and cultivars from other areas back to Polyssu and/or Alfredo Chaves, coupled with the apparent ease with which the trait can be completely transferred through phenotypic selection, implies that extreme levels of Al tolerance may be under simple genetic control. Although some studies do support that prediction, we still lack a clear and comprehensive picture of Al tolerance genetics in wheat, even after decades of research into the topic. In part this can be attributed to the fact that over the years, genetic studies have varied widely in choice of genotype(s), although the tolerant standards for comparison often include Atlas 66 or BH1146. Further, these studies rely upon a diverse array of screening media and methods and Al levels with which to assess genotypes [3]. Thus, it is difficult to assemble the results into a cohesive picture of Al tolerance. Regardless of this obstacle, certain results do provide a foundation on which to begin to describe the genetic basis for Al tolerance in wheat.

Perhaps the earliest attempts to describe Al tolerance inheritance in wheat were conducted by Iwar Beckmann, one of the scientists behind the development

of the early Al-tolerant Brazilian cultivars. He observed that F_2 populations derived from Al-tolerant versus Al-sensitive cultivars segregated 3:1 for tolerance as expected for a single dominant character, although he noted that there were many plants scored as "doubtful" as well [15]. Since then, many other studies have confirmed that, unlike tolerance to other soil-associated abiotic stresses such as salt toxicity, single major genes that confer a high degree of Al tolerance do exist in wheat.

The first inheritance study of Al tolerance in wheat to be formally reported in the literature was by Kerridge and Kronstad [34]. In an experiment elegant in its simplicity, they crossed the Al-tolerant wheat cultivar Druchamp and the Al-sensitive cultivar Brevor and analyzed the F_2 population from this cross for root growth in hydroponic conditions in the presence or absence of Al. In its absence, the F_2 population exhibited a rather narrow and continuous distribution for root growth with the mean approximately intermediate between the two parents. However, when a second set of F_2 plants was grown in the presence of Al in the solution, a distinct bimodal distribution emerged, with approximately one fourth of the plants now exhibiting extremely limited root growth and being separated from the remaining three fourths of the plants by a clear discontinuity in the distribution curve. This characteristic 3:1 ratio of Al-tolerant versus Al-sensitive plants strongly supported the hypothesis that Al tolerance differences in the F_2 were due to segregation for a single dominant gene. Later studies using hydroponic culture root measurements or other methods of assessing Al tolerance such as hematoxylin staining or acid soil growth bioassays have also confirmed the presence of major Al tolerance genes in populations segregating for Al tolerance [24,35–38]. Although these studies have generally used different tolerant and sensitive cultivars, in some instances the inheritance of the same cultivar has been examined by different groups in crosses with different Al-sensitive lines, and results have been consistent. For instance, different studies with the highly Al-tolerant cultivar BH1146 have suggested that its tolerance, or a large part of it, derives from a single major locus [24,36].

Whereas many studies have reported that Al tolerance follows a simple inheritance pattern, other studies have shown Al tolerance to represent the expression of two genes. The cultivar Atlas 66, an Al-tolerant cultivar developed in North Carolina and released in the 1940s, has more than once been suggested to possess more than one Al tolerance gene. This is based upon a 15:1 segregation for Al tolerance versus Al sensitivity in F_2 populations from crosses between Atlas 66 and Al-sensitive wheat lines [36,37,39], although single-gene segregation was also observed depending on the sensitive parent used. This suggests that two dominant genes are present in Atlas 66 that can each confer Al tolerance. The fact that Al tolerance was conferred whether one or both genes were present in plants of the F_2 population suggests that these genes do not act in a completely additive fashion. An examination of the pedigree of Atlas 66 indicates that the highly Al-

tolerant cultivar Frondoso was the likely donor of Al tolerance to Atlas 66. Frondoso traces its pedigree back to the Polyssu × AC crosses from early in the 20th century, which suggests that the Al tolerance of Atlas 66 also derives from these old Brazilian cultivars. Other studies have also reported digenic segregation in a population derived from an Al-tolerant versus Al-sensitive cross but with gene interactions [35]. Furthermore, the presence of more than one gene in a given Al-tolerant cultivar can be inferred from studies in which backcross introgression of Al tolerance from an Al-tolerant cultivar to an Al-sensitive cultivar has resulted in incomplete transfer of the trait [40,41].

Although these studies have provided insights into the genetics of Al tolerance, they simultaneously expose a paradox that has long faced scientists seeking to understand the genetics of Al tolerance—namely that Al tolerance is commonly inherited in a simple fashion in designed crosses; yet, as noted earlier, when Al tolerance is evaluated in a range of germ plasms, a broad and continuous distribution from highly tolerant to highly sensitive genotypes is observed, indicative of a complex multigene system with varying effects on Al tolerance. Thus, it is difficult to reconcile such findings with a generic genetic model in which one or a few loci control Al tolerance in wheat. To this day, this paradox represents a major unanswered question in Al tolerance genetics.

To examine further the issue of gene diversity for Al tolerance, it should first be recognized that the genetic basis of Al tolerance determined from an Al-tolerant × Al-sensitive cross can provide only limited insight into this issue, primarily because inferences are restricted to the cross in question. Instead, explorations of Al tolerance gene diversity can be adequately addressed only by genetic studies that either directly determine on a case-by-case basis whether Al tolerance between two Al-tolerant cultivars is due to the action of the same or a different locus or by statistical methods associated with quantitative genetics. In some instances, this has helped further our understanding of the genetic basis of Al tolerance, whereas in other instances it has revealed contradictory information.

Some efforts have been made to determine whether different Al-tolerant cultivars possess the same or different genes for Al tolerance. The ability to trace the pedigree of most highly Al-tolerant cultivars back to either Polyssu or one of the AC lines developed in Brazil, coupled with the ease with which this trait has been introgressed into other germ plasm, implies that highly Al-tolerant lines are likely to share a gene or a few genes for Al tolerance. By crossing these different Al-tolerant genotypes and examining derivative segregating populations for individuals that exhibit greater Al sensitivity than either parent (transgressive segregation), it is possible to determine whether the genes in the parents are in fact the same or different. In some instances, results of such studies imply that the same gene for Al tolerance is present in the different Al-tolerant genotypes being evaluated in this fashion because no progeny exhibiting less Al tolerance than the parents were found [41,42]. However, Camargo [36] reported that when BH1146 and

Atlas 66 were crossed and F_2 progeny analyzed at an Al level at which both parents are tolerant, digenic segregation was observed, implying that these two highly Al-tolerant cultivars possess distinct Al tolerance genes that were both segregating in the F_2 population. Thus, there appears to be some firm evidence that different genetic loci contribute to Al tolerance differences in wheat, but the number of such genes remains unknown.

An additional source of Al tolerance variation in wheat that could represent an additional layer of complexity is allelic variation within a given locus. It would seem surprising to find that significant levels of allelic variation could have evolved since the domestication of wheat. Indeed, molecular genetic studies have generally revealed that quite low levels of DNA sequence polymorphism exist in wheat. Nonetheless, allelic variation does exist for other traits, so it is not unreasonable to assume that such variation may extend to Al tolerance genes. Allelic variation for Al tolerance genes has been reported for both barley and maize, where multiple allele series of the same gene encode varying degrees of Al tolerance among cultivars [43,44]. In wheat this has not been definitively established, but it is interesting to note that the Al tolerance gene Alt_{BH} from the highly Al-tolerant cultivar BH1146 and Alt2, a gene from the less tolerant Chinese Spring, reside at roughly the same position on chromosome 4D [24,45]. We might suggest that these genes represent alternative alleles of a common locus, but we have only just begun to explore this issue.

In summary, significant levels of genetic variation for Al tolerance exist in wheat and have been exploited in breeding programs to improve productivity on acidic soils with chronic Al toxicity problems. Aluminum tolerance is not an intrinsic feature of wheat but rather is likely to have arisen by mutation during the course of its evolution, after a series of polyploid events resulted in the creation of its hexaploid genome. Extreme levels of Al tolerance in wheat can usually be traced back to a select few ancestors of Brazilian origin and appear to be under rather simple genetic control. This source of Al tolerance has been used worldwide to improve wheat production on acidic soils. However, the broad distribution of Al tolerance observed among wheat cultivars as a whole suggests that a simple genetic model does not adequately explain Al tolerance variation in this crop. This continuous variation is likely to be due to the presence of multiple genes that have evolved independently, multiple allele series for these genes, interactions between loci, or combinations of all of these factors.

4 MOLECULAR GENETICS AND MOLECULAR BIOLOGY OF ALUMINUM TOLERANCE

As we enter an era in which the tools of molecular biology present extraordinary opportunities to address questions in biology, many such opportunities also exist for exploring the genetic basis of Al tolerance. Obtaining answers to these ques-

tions is not only of interest for basic biological reasons but may have quite broad significance for crop improvement on acid soils. Over the past several years, a few studies involving molecular approaches to improve Al tolerance have been conducted.

This activity is not disconnected from the explosion of research focused on generating molecular maps of crop plants. An array of different methods for generating these maps has become available [46–49], and now the generation of such molecular maps is routine and, from a technical standpoint, not particularly demanding. As for other major crops, much effort has been directed at the generation of molecular maps of wheat (for example, see GrainGenes web site, http://wheat.pw.usda.gov/). From a practical standpoint, these maps have found their greatest application in the identification of molecular markers for genes encoding traits of agricultural importance. Even a cursory review of the current applied plant genetics literature will reveal the diversity of research efforts seeking to identify markers for genes involved in disease resistance, quality, and abiotic stress tolerance, including Al tolerance.

To date, two separate studies have identified molecular markers for Al tolerance genes in wheat. Riede and Anderson [24] identified marker loci for the gene Alt_{BH}, which confers a high degree of Al tolerance in the Brazilian wheat cultivar BH1146. Segregation for Alt_{BH} was scored as a discrete Mendelian character by root hematoxylin staining of Al solution-grown recombinant inbred lines from the cross BH1146 × Anahuac. Single-gene control was indicated by the 1:1 segregation ratio and was confirmed with root growth measurements. Restriction fragment length polymorphism (RFLP) mapping located Alt_{BH} on the long arm of chromosome 4D. The marker most tightly linked to Alt_{BH} was the locus *Xbcd1230,* which was approximately 1 centimorgan (cM) from Alt_{BH}, whereas the marker locus *Xcdo1395* was approximately 10 cM from Alt_{BH}. When Al tolerance segregation was treated as a metric variable rather than as a discrete variable using actual root growth data, *Xbcd1230* accounted for 85% of the phenotypic variance for Al tolerance. Thus, Alt_{BH} contributed virtually all of the Al tolerance to BH1146, with the residual variance presumably due to environmental effects and/or segregation for minor genes influencing root growth independent of Al.

In another study, Luo and Dvorak [45] used hematoxylin staining to map a gene conferring Al tolerance in the landrace Chinese Spring. Scored strictly as a Mendelian character, this gene (designated *Alt2*) was also mapped by RFLP analysis to the long arm of chromosome 4D, a location consistent with results of analyses of Al tolerance in Chinese Spring cytogenetic stocks [50,51]. Because Chinese Spring has less Al tolerance than BH1146, *Alt2* is not the same gene as Alt_{BH}, but it may represent an alternative allele of the same locus that conditions less Al tolerance. This hypothesis is bolstered by the inference from hematoxylin staining results that each gene appears to confer Al tolerance by excluding Al from the root apex [24,45].

The most obvious use of such markers (particularly those identified for Alt_{BH}, a gene with potential importance to breeding programs) would appear to be as a tool for marker-assisted selection of Al tolerance. However, the adoption of molecular markers for this purpose may be of questionable value because other rapid, inexpensive, and simple methods for evaluating Al tolerance in wheat are available, as previously discussed, and have been used successfully by breeding programs to select for Al tolerance (summarized in Ref. 3). However, marker-assisted selection for Al tolerance may be justified by the preexistence of a marker-assisted selection program for other traits or when it would be cumbersome to undertake a specific selection program for Al tolerance because it might impede screening and selection for other important traits, such as seedling selection for disease resistance. Also, bioassays conducted on juvenile plants in nutrient solution culture or in soil media under controlled conditions do not have the full predictive value of mature plant performance in the field. A marker-assisted selection program might be developed to bypass these forms of selection and to apply selection pressure for other traits critical to acid soil tolerance, such as phosphorus use efficiency.

An additional use of such molecular markers will be to help resolve questions about Al tolerance gene diversity in wheat. As additional molecular mapping data become available, a more comprehensive picture of gene number versus allele diversity in this species will be acquired. Should mapping data ultimately reveal the presence of distinct Al tolerance loci among wheat cultivars, it may be possible to use the molecular markers to pyramid different Al tolerance genes in a single genotype and thereby obtain additive enhancement of Al tolerance. The potential for gene pyramiding to obtain increased Al tolerance can be inferred from some studies that have shown that backcross breeding, which is often used to transfer a single desired gene from one cultivar to another, may result in incomplete Al tolerance transfer from a tolerant cultivar to a sensitive one [40,41]. This suggests that Al tolerance genes may have an additive effect in certain instances that can be exploited to enhance Al tolerance.

Molecular mapping studies have provided additional scientific insight into more basic questions associated with Al tolerance. Within the last decade, it has been established that chromosome structure, and thus gene order, among related plant species, including the domesticated grasses, is conserved [52]. Because gene order is conserved among members of the domesticated grasses, cross-species comparative molecular mapping of Al tolerance genes can be used to address the question of interspecific Al tolerance gene conservation, i.e., do different species rely upon the same or different genes to obtain Al tolerance? Comparative mapping provides a means for answering this question. To date, limited data exist on chromosome locations of Al tolerance genes in other species, but hypotheses are beginning to form regarding interspecific Al tolerance gene diversity. For instance, Minella and Sorrells [53] used trisomic analysis to determine that a major

Al tolerance gene in barley, *Alp,* was located on chromosome 4. Because barley chromosome 4 is homeologous to the wheat group 4 chromosomes, this suggested the possibility that *Alp* and the wheat Al tolerance genes Alt_{BH} and *Alt2* on the long arm of wheat chromosome 4D are orthologous.

Recently, a study in one of our laboratories [54] identified molecular markers for *Alp*; this gene was found to reside on the long arm of barley chromosome 4, which is homeologous to the long arm of wheat chromosome 4D. Further, *Alp* was found to be linked to *Xcdo1395,* which is also linked to Alt_{BH} in wheat [24]. *Alp* was approximately 2 cM from *Xcdo1395,* and Alt_{BH} was reported to be approximately 10 cM from the same RFLP marker locus in wheat. This quantitative difference in linkage intensity could be due to an apparent chromosome rearrangement, positioning *Alp* and *Xcdo1395* closer to the centromere than Alt_{BH} and *Xcdo1395* are in wheat, thereby causing suppressed recombination between the two loci in barley. This conservation of linkage between *Xcdo1395* and both Alt_{BH} and *Alp* strongly indicates that these two Al tolerance genes are likely to represent orthologous loci and that independent mutations at this locus underlie natural variation for Al tolerance in both species. Additional mapping of Al tolerance genes has also been conducted in rye, where markers have been identified for major Al tolerance genes on rye chromosomes 6R and possibly 4R [55]. Interestingly, rye chromosome 4R has a segment syntenic with the Triticeae group 4 chromosomes [56], raising the possibility that in the tribe Triticeae—which includes wheat, barley, and rye—Al tolerance will consistently be found to be partly or wholly explained by parallel mutations in orthologous loci. Thus, gene discoveries in one species may accelerate gene discoveries in others.

Although the question of Al tolerance gene diversity is of basic interest, it also has broad practical implications for further genetic improvement in wheat and other species. If gene identity is found to be conserved across species, one may view the genes in different species as an extended allele series spanning species boundaries. This implies the possibility that if such a conserved Al tolerance gene can be cloned from a highly Al-tolerant plant and transferred intact into a less tolerant plant known to possess a less effective ortholog, the introduced donor gene could be expected to act as a new allele of this locus, resulting in a level of Al tolerance commensurate with the level conferred by the gene when present in the donor species. In contrast, if unique tolerance genes are identified in different species, their cloning would present the opportunity to pyramid these genes within any given crop by genetic engineering as a means to increase Al tolerance.

The isolation of an Al tolerance gene from wheat has been a goal of scientists for many years. Efforts to clone Al tolerance genes from wheat date back nearly a decade and first involved studies to identify the protein products of such genes. The identification of a protein can serve as a starting point for working backward to isolate the respective gene encoding it. In 1991, a number of independent groups reported on such attempts. Delhaize et al. [57] and Picton et al. [58] de-

scribed polypeptide differences in root apices of Al-tolerant versus Al-sensitive cultivars. Delhaize and coworkers used the Al-sensitive Egret and the Al-tolerant Carazinho, while Picton and coworkers used Warigal as their sensitive standard and the tolerant cultivar Waalt. Using two-dimensional (2-D) electrophoresis, each group identified constitutive differences in polypeptide profiles between the cultivars being compared in the absence of Al. Furthermore, they both reported that Al exposure induced polypeptide synthesis in both cultivars as well, including a few polypeptides preferentially induced in the Al-tolerant cultivars. The polypeptide differences present in the tolerant lines, but not the sensitive lines, were considered as possible Al tolerance gene products. However, when Delhaize and coworkers examined Al-tolerant versus Al-sensitive sister lines derived from a cross between Egret and Carazinho, none of the polypeptide differences present in Carazinho were consistently associated with the presence of Al tolerance or its absence, indicating that they are not encoded by the Al tolerance gene itself.

Similar studies were conducted by Ownby and Hruschka [59] and by Basu et al. [60]; however, one notable difference is that they actually attempted to partition the root tip polypeptides into microsomal (membrane-associated) and cytoplasmic fractions to obtain more specific information on the cellular locations of the polypeptides. As in the previous studies, various polypeptides were found to accumulate during Al stress, and in some cases differential expression between tolerant and sensitive cultivars was observed. Follow-up research by Cruz-Ortega and Ownby [61] classified one of the proteins that they had previously identified on 2-D gels as being induced under Al stress as similar to pathogenesis-related proteins, based on protein sequence data. However, because this polypeptide is induced in both Al-tolerant and Al-sensitive cultivars, it is unlikely to represent a true Al tolerance gene product. Taylor et al. [62] and Basu et al. [63] demonstrated that a 51-kDa polypeptide and a 23-kDa polypeptide, induced upon Al exposure in Al-tolerant wheat cultivars appear to cosegregate with the Al tolerance phenotype in segregating populations. The 23-kDa polypeptide is exuded by roots and has Al binding activity [63]. This is an interesting finding, but it remains to be seen whether the gene encoding this polypeptide is also linked genetically with Al tolerance segregation, which would strengthen the possibility that the polypeptide may indeed be an Al tolerance gene product. Thus, despite a number of attempts, a protein-based strategy for isolating a bona fide Al tolerance gene has not been successful. However, given the dramatic analytical improvements in protein analysis methods that have developed with the maturation of proteomics as a scientific discipline, such a strategy may eventually be fruitful.

In addition to protein-based studies, several attempts have been made to clone Al tolerance genes by molecular methods. This has included a number of studies that have approached the problem by searching for genes that exhibit increased expression upon Al exposure. The first of these attempts to be reported was by Snowden and Gardner [64]. Using differential complementary DNA

(cDNA) screening of a root tip cDNA library from Al-stressed roots of the Al-sensitive cultivar Warigal, they isolated five cDNAs representing genes whose expression is induced by Al exposure. Constitutive expression of four of the five genes in the absence of Al was higher in the Al-tolerant cultivar Waalt than in Warigal. Interestingly, four of the five genes exhibited reduced levels of expression in Waalt when exposed to nontoxic levels of Al, whereas when toxic levels were used, the same four genes exhibited an increase in transcript abundance. Two of the cDNAs exhibited sequence homology to other genes; one was similar to metallothioneins, and the other encoded the enzyme phenylalanine ammonia lyase [64]. Later research by the same group identified two additional genes whose expression is increased upon Al exposure, one of which was similar to asparagine synthetase and one similar to Bowman–Birk proteinase inhibitors [65]. Similarly, in follow-up research on their earlier protein studies, Cruz-Ortega et al. [66] identified a β-glucanase and a fimbrin-like gene that were each up-regulated in root tips by Al exposure; the fimbrin-like gene is interesting because it plays a role in cytoskeletal formation, and the cytoskeleton has been suggested to be affected by Al toxicity in cells [67]. Hamel and coworkers [68] isolated several Al-induced cDNAs from the root tips of the Al-tolerant cultivar Atlas 66, including genes for peroxidase, cysteine proteinase, and oxalate oxidase.

Tests of the ability of certain of these genes to confer Al tolerance have been conducted by expressing these genes in plants and determining whether they confer an increased measure of Al tolerance. Ezaki and coworkers [69] reported on results of experiments in which they transformed *Arabidopsis* with a series of different Al-induced genes identified in several plant species, including one gene, a Bowman–Birk protease inhibitor, recovered from wheat [64]. Overexpression of this wheat gene was not found to increase Al tolerance of *Arabidopsis* plants. However, overexpression of a few of the other genes from other plant species did increase Al tolerance, although not dramatically and only across a narrow window of Al concentrations. Interestingly, two of these genes also conferred Al tolerance in yeast [70]. But it was suggested that this is due to an increase in basal stress tolerance and not to an increase in Al tolerance per se.

Thus, to date none of the genes recovered during the course of any of these molecular cloning efforts is likely to be a bona fide Al tolerance gene. Perhaps this is due to the fact that if one looks at the physiological mechanism of Al tolerance in wheat (Al-inducible malate release from the root apex), the response is induced within minutes of exposure to Al [71]. This suggests that the genes that encode the cellular machinery necessary for the Al tolerance response are constitutively expressed but that the mechanism of Al tolerance that this machinery encodes is rapidly activated at the biochemical level upon perception of Al. Therefore, Al tolerance genes in wheat and perhaps other plants may not actually exhibit induced expression at the molecular level, so differential screening methods that have been widely used in the aforementioned studies may not be appropriate for Al tolerance

gene isolation. Nonetheless, some of the genes that have been identified in this fashion may play a role in cellular adaptation associated with the Al tolerance response itself; presumably the efflux of large amounts of malate from root tips could cause metabolic changes for which the cells would need to compensate.

Perhaps it is unfortunate that wheat has served as such a useful model for genetic and physiological research on Al tolerance because its polyploidy and large genome make it difficult to make the subsequent transition from these types of studies to complementary molecular biological research aimed at isolating Al tolerance genes. However, in the future it may be possible to undertake Al tolerance gene cloning efforts in a diploid relative of wheat with a small genome, such as rice (*Oryza sativa* L.), that is amenable to certain methods such as positional cloning and then use the resultant cloned genes to recover wheat homologs through traditional molecular methods. It therefore seems inevitable that within the next 3 to 4 years, Al tolerance genes from wheat and other plant species will be isolated, which will provide new insights into our understanding of this important trait and will offer novel opportunities to improve the productivity of crops grown on acid soils.

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15

Managing Soil Acidification Through Crop
Rotations in Southern Australia

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1 INTRODUCTION

Wheat-based farming is the dominant production system in the 250- to 600-mm
rainfall areas in Australia. This type of farming may use a pasture–ley, a phase
system, or a continuously cropped system [1]. The ley system has short annual se-
quences of cereal crops separated with either short or long periods of legume-
based pasture. With the phase system, the crop sequence is longer and can include
pulse and oilseed crops as well as the cereals. Whatever the sequence of crops and
pasture, the overarching farm objective is to provide an appropriate soil environ-
ment so that profitability is ensured without negatively affecting long-term sus-
tainability. Farmers seldom follow strict rotations; rather, they develop flexible
crop and pasture sequences based on rules that account for short-term goals and
long-term environmental considerations. The rotations used must ultimately be
consistent with providing a base for nitrogen and phosphorus fertility, an adequate
soil structure associated with maintaining organic matter, and disease, pest, and

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weed management. In all cropping regions there has been a trend toward increasing the cropping component in the rotation, assisted by reduced tillage systems, more retention of crop residues, and also an increase in nitrogen fertilizer use.

Soil acidification is recognized as a serious form of land degradation associated with crop rotations. In southern Australia, the acidification in farming systems that use rotations of crops and pastures is well studied, particularly in higher rainfall areas. In these crop rotations, the N cycle and C cycle contribute most to the acid input [2,3]. Application of lime is the main management option used for correcting the acidity caused by acidification. Although lime can change the chemistry of the top 5 to 8 cm of the soil and provide immediate benefits to crop production, it is also important that the crop–pasture rotation is managed so that further acid addition to the soil is minimized. In particular, attention has to be given to the way nitrogen and carbon are managed within the crop rotation.

What is clear from studies on acidification occurring in crop rotations is that much of the accelerated acidification is associated with nitrogen inputs into the farming system in excess of the needs of the plant [4,5]. Depending on the growing season rainfall, a 4 to 5 ha^{-1} wheat crop requires about 200 to 250 kg available N ha^{-1} to satisfy herbage and grain needs [6]. The primary source of mineral N available for supplying the N for such a crop is the soil. In a given year, a small portion (about 2%) of organic N in soil is mineralized from soil organic matter, contributing mineral N amounts of 100 to 200 kg ha^{-1} [7,8]. Further, the quantity of N_2 fixed per legume year in the rotation can be about 100 kg N ha^{-1} [3,9]. However, in many situations in the crop rotation, the supply of mineral N from the soil may be insufficient to meet crop N needs, and thus fertilizer N is added to the system [10]. The ongoing problem faced by farm managers in making decisions about N requirements is ensuring that the N required for obtaining targeted grain or forage yield and protein levels is matched with the supply of N.

Acidification of soil can also result from addition of carbon acids as part of the return of organic materials to the soil and from the export of organic anions in products [11,12]. Obviously, these acidifying inputs, as well as inputs associated with optimizing crop N nutrition, are essential in maintaining productive, stable, and economic crop rotation farming systems. Therefore, an objective of acidification studies to date has been the understanding of the fluxes of both nitrogen and carbon in the soil and plant materials so that management strategies are developed that minimize soil acidification. In this chapter, we examine the agronomic management options available for use in crop rotations in southern Australia for minimizing soil acidification. These may be in addition to, but also associated with, lime use and the use of acidity-tolerant cultivars.

2 SOIL ACIDITY IN CROPPING AREAS

Acid soils are common in some parts of the sheep–wheat production areas in the southeastern and southwestern regions of Australia [13,14]. The extent of soil

acidity (pH measure) prior to the clearing of the land for agriculture was influenced by the annual rainfall and the different clay mineralogy of the soil parent material (which influences the buffering capacity of the soil). The extent to which soil acidification has lowered the pH in these areas since land clearing is similarly influenced by these factors, as well as the years since land clearing and the proportion of legumes in the rotation in that time [15].

The native vegetation prior to land clearing was dominated by deep-rooted, perennial species. With this vegetation mostly cleared, the replacement vegetation was mostly shallow-rooted annual pastures and crops. With this change, more water has drained in the soil profile. The rates of acidification are generally more pronounced in the higher rainfall areas, and soils with pH values in the range 4.8–5.5 ($CaCl_2$) are likely to be more susceptible to rapid acidification [16,17].

The higher rainfall cropping zones within Australia are the areas with an annual rainfall greater than 500 mm. There is extensive evidence of accelerated acidification affecting soils in higher rainfall cropping areas in northeastern Victoria and southern New South Wales [14,18]. These areas frequently experience deep drainage of water below the influence of plant roots [19]. The medium rainfall cropping zones have an annual rainfall between 400 and 500 mm. In Western Australia, acidification is affecting the medium rainfall cropping areas with sand over clay and sandplain soils [20,21]. In the medium rainfall cropping zone in Victoria, New South Wales and South Australia, there is evidence that soil pH has declined with crop-based farming, although there is only preliminary evidence that induced soil acidity is affecting crop production [22–24]. Finally, in the semiarid cropping regions (250 to 400 mm rainfall), acidity is not usually a problem, although in New South Wales some changes associated with the introduction of crop practices have been identified as affecting soil pH [25]. In contrast to the higher rainfall cropping zones, it is unlikely that the medium and semiarid rainfall areas would have regular deep drainage of soil water.

The poor productivity of plants grown in acidic soils can be due to combinations of soil-related toxicities (Al, Mn, H^+) as well as deficiencies of essential nutrients (P, Ca, Mg, Mo, Zn). The correct diagnosis of the major limitations associated with acidity is important because crop yields on different acid soils can be low for different reasons [26]. The relatively high concentration of Al^{3+} in the soil solution is one of the main characteristics of strongly acidic soils and depends on many soil factors, including the predominant clay minerals, the organic matter content, and concentrations of other anions [27,28]. The Al^{3+} produced by the dissolution of clay minerals under acidic conditions can displace exchangeable cations from clay and other charged colloids. The chemical reduction of Mn is also augmented under low-pH conditions and therefore toxic concentrations of Mn^{2+} can develop in some acidic soils [29].

The buffer capacity of the soil directly influences soil acidity, with various inorganic soil components as well as organic matter being the most important materials in establishing pH buffer capacity [30]. The buffering capacity of the inor-

ganic soil components is related to both the permanent lattice charge and the pH-dependent charge [31]. With soil organic matter, the pH-dependent charge is due to the dissociation of carboxylic (stronger acids) and phenolic (weaker acids) groups [32,33]. Aluminum can be associated with soil organic matter, with strong Al–organic complexes such as with fulvic acid and citric acid, which are nontoxic to plants [34,35].

The long-term effects of soil acidification on soil properties include (1) a reduction in the soil cation exchange capacity (CEC) and an associated loss of ability of the soil to store reserves of nutrient cations, (2) accelerated mineral degradation with increased concentrations of Al^{3+}, and (3) reduced soil biological activity [11]. Knowledge of the rates of acid addition and the chemical behavior of the acidity components is important as this provides the basis for agronomic management strategies for minimizing acid input in crop rotations.

3 ACIDITY IMPACTS ON CROP PRODUCTION

Lime use has been widely recommended for wheat-based farming where the soils are strongly acidic, particularly in the higher rainfall cropping areas [18,20,36]. In most situations where the soil pH was less than 4.7 ($CaCl_2$ extraction), yield responses of the order of 20–100% with wheat have been obtained after liming the soil. The evidence from a wide range of sites with different field crops, including barley and canola, both known to be acid-sensitive species, and subterranean clover, is that lime use has given consistent yield responses [18]. These responses to lime application can be due to the correction of a number of the deficiencies or toxicities of acidic soils, although the reduction in soil Al^{3+} concentration is thought to be the most likely reason for crop yield improvement [37,38]. The benefits of using cultivar tolerance to avoid potential harmful effects of acidity have also been shown in situations where the soil acidity level is severe, as well as where the acidity is less severe (pH > 4.7–5.0). It is an easy management option to use acid-tolerant species or cultivars as the choice of crop in cropping rotations. Another advantage cropping enterprises have for managing acidity is the ease with which the lime can be incorporated within the top 5–8 cm horizon with soil cultivation. Thus, it is possible with regular lime use and time (and subsequent movement of the lime effect in the soil) to influence soil pH up to 15–20 cm depth [39,40]. In such situations, it should be possible to ameliorate or avoid the development of subsoil acidity.

In the cropping regions where the soils are acidic but where there are more variable or seasonally dependent responses to lime application (e.g., medium rainfall zones), there is a need for matching of lime inputs to a target pH or at least application of enough lime to offset ongoing acidification. In these areas, similarly to the higher rainfall areas, the lime applied must be related to some measure of agricultural production or a target pH that is based on changes in soil chemistry.

An optimal liming program should not only reduce plant-available Al and Mn concentrations to levels that allow optimal production of a particular crop but also ensure adequate levels of plant available Ca and Mg and create conditions conducive to beneficial soil fauna [41].

In some situations, negative effects associated with high applications of lime have been reported. For example, decreases in wheat yields can occur due to pH effects on disease incidence [42], and in some areas in South Australia the inducement of Mn deficiency may negate any positive yield response to lime, particularly in subterranean clover [43].

4 ACIDIFICATION PROCESSES

Soil acidification is the process in which a decrease in pH is the product of the change in H^+ and the pH buffering capacity of the soil [5]. In natural ecosystems, soil acidification generally occurs over a time scale of thousands of years, but under agricultural production it can occur over a time scale of decades [4,44]. If only rainfall is considered as an acid promoter in a closed natural ecosystem, the H^+ flux in a 1000-mm annual rainfall situation at pH 5.0 would be about 0.1 kmol H^+ ha^{-1} $year^{-1}$ [45]. However, in wheat-based crop rotations in southern Australia, the rates of acidification can be 0.16 to 3.6 kmol H^+ ha^{-1} $year^{-1}$ for pastures [46–49] and 1.0 to 7.5 kmol H^+ ha^{-1} $year^{-1}$ for cereal-legume rotations [2,20,47,48,50,51]. The overall rate of acidification is dependent on the initial soil pH and buffering capacity, the time period involved, and the particular management system [17]. The N and C cycles contribute most to the acid and alkaline reactions in these rotations, with the processes involved in the generation of H^+, OH^-, and organic anions occurring independently in the soil and plant system [3–5,52,53]. The understanding of these N and C cycle processes is important as they provide background for development of nonacidifying management strategies.

Incomplete cycling of N in soils under crop-rotation management has been identified as a major cause of increasing acidity. Almost all the nitrogen in biological ecosystems exists as organic N compounds (R-NH$_2$). Given that R-NH$_2$ is the ecosystem N sink/source (the reference state for nitrogen), the addition of NH_4^+ makes the equilibrium of the reaction (R-OH + NH_4^+ → R-NH$_2$ + H_2O + H^+) shift toward the production of R-NH$_2$, and this process produces H^+. The production of NO_3^- resulting from nitrification and its accumulation in soil releases H^+, and the loss of NO_3^- accompanied by base cations leaves H^+ in the system. In a similar way, the addition of NO_3^- makes the equilibrium of the reaction (R-OH + NO_3^- + H^+ → R-NH$_2$ + $2O_2$) shift toward the production of R-NH$_2$, and this process consumes H^+ (an alkaline reaction). The production of NH_4^+ from R-NH$_2$ mineralization also consumes H^+, so its accumulation is an alkaline reaction, and the loss of NH_4^+ (export) is likewise an alkaline reaction [11]. The combined

ammonification and nitrification of R-NH$_2$ (including urea) generates 1 mole of protons for every mole of N transformed, and denitrification then can consume the protons (see Fig. 1). The ammonia volatilization process generates protons.

In a closed system where there is no net gain or loss of N associated with these N soil processes, no net generation of H$^+$ ions occurs [52,54]. However, in a crop-rotation practice, an imbalance in the amounts of N entering and leaving the soil system does occur, and this can lead to permanent soil acidification. This imbalance is due to the requirement to improve the productivity of soils, and this is done through increasing the plant available pool of N either by stimulating biological N$_2$ fixation or by the application of N fertilizers. The use of ammonia-based fertilizers, such as monoammonium phosphate and diammonium phosphate, that are frequently applied with the seed at sowing causes a net addition of acidity as they generate 2 or 1.5 moles of protons, respectively, for every mole of N, resulting in an excess balance of protons. Net acid addition can also result from the leaching and loss of NO$_3^-$ from this cycle. When NO$_3^-$ and basic cations leach from the rooting zone of the soil, there is a net cumulative H$^+$ production in the soil of one H$^+$ for every NO$_3^-$ ion leached [5,45,52]. This results in permanent soil acidification in the zone where the nitrification occurs. Thus, amounts of acidity entering and staying in the soil system depend on the relative magnitudes of these N cycling processes.

The N transformation processes are soil induced, but the N cycle also involves plant-induced processes that contribute acidity and alkalinity to the soil.
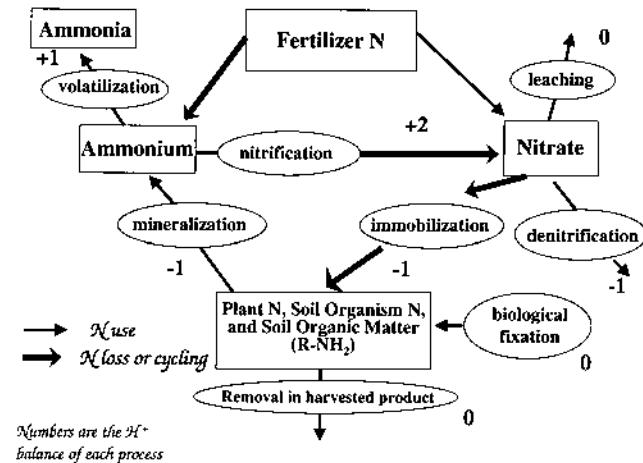
FIGURE 1 Nitrogen transformation processes that produce and consume acidity in soils.

The uptake and assimilation of N as NH_4^+ or N_2 into legume nodules lead to H^+ ion extrusion into the rhizosphere soil. The uptake of N as NO_3^- by plants results in the generation of OH^- and provides a balance to the H^+-producing processes.

Processes associated with the C cycle also contribute acidity and alkalinity, with organic anions being either removed in agricultural products or returned to the soil as plant residue or animal excreta [4,55]. The organic anions are alkalis on the assumption of conversion to undissociated acids. If the organic anions added back to the soil associate with protons to form undissociated organic acids, there is no net change in acidity. In fact, because organic acids such as carboxylic acid and phenolic acid are weak acids, there is always some part of these organic acids that dissociates to release H^+. This process increases the size of the soil H^+ pool, and thus soil acidity increases. If these reduced C compounds are then decomposed through respiration, this acidity is neutralized. However, the contribution of this process to soil acidity mainly depends on the nature of organic acids and the environment pH, and usually the decomposition of organic acid groups is slow compared with the dissociation process, so the outcome is an increase in acidity [56].

These H^+ balancing processes are spatially compartmentalized between the soil and the plant and are linked through the plant uptake of highly mobile NO_3^- and the return of organic N to the soil. A crop or pasture may remove alkalinity from the bulk of the soil during the growing season and partially recycle this alkalinity to the soil surface when the crop residues are retained. Therefore, acidification of soils is likely to be separated temporally as well as spatially because of this compartmentalization of acidifying and alkalizing processes between soil and plant [11]. In some years, the net result will be that the soil is alkalizing, and in others years it will be strongly acidifying. For example, in the long-term study undertaken at Wagga Wagga (rainfall 540 mm), the first wheat crops in a wheat-dominated rotations were alkaline, subsequent wheat crops were mildly acidifying, and pastures in these rotations were strongly acidifying. The overall trend with time for the soil volume in this experiment was acidic [3]. In this study, most of the N leached below 30 cm was recovered within the same or the subsequent years, but drainage events did occur. Drainage losses can be highly episodic and can occur in medium rainfall cropping regions and even in semiarid regions [57,58]. Agronomic solutions for reducing drainage below the rooting zone will not always be possible. Given that farmers in southern Australia have been using high rates of N fertilizer (80 to 120 kg N ha^{-1}) over the past decade, it is likely that soils are accumulating large amounts of mineral N [38,59] and also have a significant redistribution of NO_3^- from the surface to depth. This uncoupling of the H^+ balance will result in stratification of acidification between soil layers. Thus, irrespective of the episodic drainage events, the net result is the accumulation of acidity in layers within the soil profile.

5   MANAGING SOIL ACIDIFICATION

5.1   Efficient Use of Soil Nitrogen and Water

The greatest scope for retarding acidification in the high and medium rainfall cropping areas is through more efficient use of soil nitrogen and water. The cropping season in southern Australia commences in autumn, when sufficient rainfall is available for establishing winter crops. The low temperatures in winter slow crop growth, but then crops grow rapidly in spring and mature in late spring or early summer. Although summer rainfall can occur, its effectiveness is negated by high evapotranspiration [60]. The inclusion of legumes (either pasture or crop legumes) in crop rotations in southern Australia is essential for maintaining soil organic matter, weed and pest management, and soil biodiversity [1]. A legume pasture annually adds from N_2 fixation about 25 kg mineral N per tonne of pasture dry matter (DM) produced [61]. Various management practices, such as winter cleaning or spray topping, are recommended in all cropping areas, particularly in the year prior to cropping, to promote pure legume swards [9,62,63]. This is done not only to optimize legume N_2 fixation but also to remove the pasture grasses that are alternative hosts to cereal root diseases, such as cereal cyst nematode and take-all. Similarly, a year of growing a crop legume can contribute high N inputs (20 kg mineral N per kg DM [64,65]). During the dry and warm summer and early autumns that are common in southern Australia, there is a buildup of mineral N from plant residues and soil organic N. In such situations, it is common that 70–100 kg mineral N ha^{-1} can be stored in the soil profile in autumn (mainly in the NO_3^- form) [8]. Also, it has been shown that drainage can occur regularly in the regions where annual rainfall is greater than 500 mm [3,19,66]. This is the situation most likely to produce high rates of NO_3^- loss, particularly when the rainfall allows rapid recharging of the soil profile and subsequent drainage of the NO_3^- below the reach of plant roots. Drainage events are also likely to occur in the less than 500 mm rainfall regions, albeit at a much reduced frequency.

Given that movement of NO_3^- is linked to soil water movement, it is essential at this time, prior to the onset of winter rains, that the soil profile is managed so that a water deficit exists. The capacity to hold NO_3^- in the soil depends on rainfall as well as on soil hydraulic characteristics. Recharge typically ranges between an average of 20 to 40 mm in the semiarid areas and 60 to 100 mm in the higher rainfall areas [19]. If the pasture phase has been based on annual species, it is possible that the soil profile is relatively full following the dry summer months. Based on the estimates given by Whitfield [67] and Smith et al. [68], there is a potential capacity for the storage of water in the soil of about 100 mm (in a 1–3 m depth) at the beginning of the winter season. A way therefore to minimize opportunities for leaching of NO_3^- is to create water deficits, thus regenerating this soil storage capacity. This can be done by using either out-of-season crops/pastures or seasonal crops/pastures with active root systems that remove water from depths beyond the

roots of annual crops and pastures. For example, deep-rooted perennial pastures, such as alfalfa, cocksfoot, and phalaris, that actively grow through the dry summer months could be used as sinks for a few years accumulation of excess water [19]. Similarly, dryland crops such as grain sorghum can also use water stored deeper in the soil when grown in the summer months [69]. Passioura and Ridley [19] suggest that such management strategies could create a storage capacity for holding about 3 years worth of drainage beyond 1 m. In much of the southern Australian cropping zone, this storage could range from 1 to 5 years depending on seasonal rainfall.

Some forage crops or grass-based pasture may be used as an effective sink for nitrogen within the growing season [11,70]. However, with the crop rotations used in southern Australia, the usual practice is to try to utilize soil available N for improving crop production. The objective must be to maximize crop growth and root activity for the full extent of the growing season. An option is early sowing of crops in the autumn that could lead to more complete absorption of soil NO_3^- before it is leached below the root zone with heavy winter rains [11]. Within the growing season, crops with more vigorous development of roots (e.g., cereals and canola compared with legumes) may be preferred for their more effective utilization of seasonal rainfall. Helyar et al. [3] described a situation where most of the N that leached below 30 cm was recovered within the same or subsequent years. Angus [71] has shown that wheat is able to reach NO_3^- deep in the soil profile late in the growing season. In the study described by Helyar et al. [3], the N input was only from the biological N_2 fixation associated with the legume pasture in the rotation. This study did not include nitrogen input from fertilizer N and thus does not reflect the high-N regimes utilized in current crop rotations. As mentioned previously, long periods of legume-dominant pasture and higher soil N concentrations brought about by high-N fertilizer inputs (often greater than 100 kg N ha^{-1} annually) would be expected to increase the reserves of N in the soil profile. Where flows of water do extend beyond the reach of the roots of annual plants, permanent acidification will result. The management of soil water to try to create net deficits is essential to optimize opportunities for capturing this soil N in either grain yield, protein, or forage.

An overall improvement in soil physical, chemical, and biological conditions that stimulate root activity and rooting depth will also increase the efficiency of NO_3^- utilization and restrict loss by leaching. There are some situations in which systems with high nitrogen use are not experiencing ongoing acidification [46]. Liming the soil does improve conditions for root elongation deeper in the soil profile, and the higher yields obtained reflect improved water use and N use efficiencies [72]. Soil improvement practices, such as deep ripping the soil to break a hard compacted layer, gypsum use to improve hard-setting surface problems, and a reduction in tillage, can also improve yields on acidic soils [73–75]. Appropriate crop rotation not only improves the soil N fertility, especially where legumes are in-

volved, but also improves soil physical properties and reduces the incidence of insects, diseases, and weeds, thus improving the likelihood of optimizing crop water use efficiency [76]. Improved tillage strategies will be part of an appropriate agronomic package for management to minimize leaching losses. Maintaining crop residues (e.g., cereal straw) on the soil surface, in stubble-retained systems, may reduce the amount of N mineralized in comparison with a cultivated or stubble-incorporated system. But, overall, the use of no-tillage practices continuously will result in a concentration of nutrients in the surface of the soil and the alkalization of this layer, and this will potentially give a net acidification deeper in the soil. The main benefit of reduced tillage and stubble-retained crop management for minimizing acidification is that more cropping years in a crop–pasture rotation are possible. This provides the opportunity for more years in the rotation of crops where there may be a net annual alkalization of the soil [12].

5.2 Fertilizer Selection

Nitrogen fertilizer is now being used extensively to improve productivity in wheat and oilseed crops in most cropping regions in southern Australia. Many farmers, prior to establishing their crop, utilize soil tests to estimate the available soil N and the need for supplementary N input as N fertilizer. Frequently, N fertilizer is used in cereal and oilseed crops following pulse crops and pasture, which is an indication that the supply of N from soil sources is often much less than the anticipated demand from high-yielding crops. The choice of N fertilizer for farmers is based on price and method of application. The ammonium sulfate and phosphate, urea, and ammonium nitrate forms of N fertilizer are the least costly per unit of N. The form of N fertilizer strongly influences soil acidification rates [77,78]. There is an inevitable acidification caused by use of the ammonium forms (monoammonium phosphate and diammonium phosphate), even without leaching. There is also potential for acidification associated with NO_3^- leaching or loss in products for these fertilizers and nearly all other forms of N fertilizer (e.g., urea, ammonium nitrate, ammonium sulfate). When N fertilizer such as urea is nitrified, one net H^+ ion is generated per N atom. These H^+ ions can be neutralized only if the entire NO_3^- product is taken up and assimilated into plant organic N, and the subsequent plant organic anion that is produced upon decomposition of the plant residues neutralizes the remaining H^+ ions in the soil. All the N has to return to the input form (NH_4^+) for neutrality. If organic matter accumulates, the NH_4^+-fertilized system can generate in excess of one H^+ per atom of N, and this is in addition to the acidity produced from the leaching and removal of product. Thus, the use of N fertilizer has the potential not only to produce permanent acidity but also to affect the magnitude of acid input into the soil volume [79].

Given the requirement of farmers for a continuing yield productivity gain, the use of N fertilizer is probably going to increase in the future throughout the

crop rotation. To avoid accumulating mineral N in the soil, farmers should be planning to use the minimum N fertilizer needed for optimal growth, yield, and protein. Methods for establishing target crop yields, such as the approaches that define a potential yield based on growing season rainfall [80], can be used in determining a nitrogen budget. The N requirement of the crop can be estimated to correspond to the target yield. In most cropping regions in Australia, reasonable predictive soil tests for nitrogen are available [81,82]. These soil test figures can be used as an estimate of available soil N and, when matched against the predicted N demand by the crop, the amount of N fertilizer required for achieving the target yield and protein is known. However, despite recent improvements in predictions of both crop yield and minimum N fertilizer requirement, these predictions can be difficult at the farm level. This is because of the unpredictable climatic parameters that determine plant growth and soil N availability and also to some extent lack of knowledge about mechanisms governing N cycling.

The average response to N fertilizer is characterized by a plateau and a point of optimal return on investment that precedes the point of maximum yield response [83]. Once the maximum rate of N input is reached and with no further yield increase, there is inevitable NO_3^- accumulation and risk of leaching if there is an excess of available N for the requirements of the plant. To obtain maximum benefits from N fertilizers, it is important that they be applied at a time when the N is used most effectively by the plant. Nitrogen supply is needed early in the growth of a wheat crop in order to establish a high yield potential, mostly through the establishment of an adequate number of tillers and then fertile heads per plant. A common practice is to use the ammonium forms of N fertilizer with the seed at sowing to promote early crop vigor and tiller development. This is an acidifying practice. Deep placement of N fertilizer can be an effective strategy for increasing yield and for avoiding placing the fertilizer with the seed. Deep banding creates a zone of lower soil strength deeper in the soil and, combined with a concentration of nutrients placed at the base of this zone, encourages plant roots to grow to greater depth where there is often more soil moisture (and a higher chance of finding nutrients). Also, there is a need for a continuing supply of N to at least the boot stage in wheat to ensure the survival of tillers and the realization of the established yield potential. For this, certainly the best timing for application of N fertilizer is within the first 6 weeks after sowing.

In the southern Australian environment, where seasonal rainfall is variable and unfavorable seasons are often experienced, the regular use of N fertilizer involves a degree of risk of poor N use efficiency. Efficiency of N uptake in southern Australia varies widely from about 40 to 80%. The efficiency of N fertilizer with dryland crops can be improved by taking care with timing and placement of application [59]. Deferring or splitting the application allows some flexibility and reduces the risk. Some knowledge of the likelihood and extent of seasonal rains is required, and reasonably reliable predictive information can

now be obtained. Therefore, in favorable years, the rate of N can be increased, whereas in dry years it could be decreased or not applied at all. Topdressing as a tactical response to a favorable season, or a predicted rain event, can greatly increase yield and protein responses compared with using applications based on set recommendations [59]. In commercial practice, crop growers are faced with the need to obtain maximum yield return for the money spent on N fertilizer while also achieving the protein or oil requirements appropriate to various premium grades. Although the overall objective is to gain the most economic return from N fertilizer, the tailoring of the N fertilizer regime to match absorption capacity for N by the plant will also help to avoid high soil N levels and the risk of NO_3^- accumulation or leaching.

The NO_3^- fertilizers such as $NaNO_3$ and KNO_3 cause an alkaline outcome when taken up by plants but are not used in broad-scale cropping because of the high cost per unit N. Similarly, slow-releasing forms of N fertilizer (e.g., metal ammonium phosphate, guanylurea, polyolefin-coated fertilizers) and inhibitors of nitrification in soils [e.g., 2-chloro-6-(trichloromethyl)pyridine (N-Serve)] can also have positive effects by slowing acid input but are not used in crop rotations because of cost [53].

5.3 Plant Selection

Large responses in plant yields can be obtained by the use of crop and pasture plants with tolerance to acidity when compared with less tolerant plants grown within the acidic cropping areas in Australia. In some situations, even the species and variety with tolerance to acidity are affected by the extent of acidity [39,73,84]. The use of acid-tolerant crops and pastures is a low-cost input on farms that is easily adopted and can often change the cost/price ratio to values more favorable for initiating lime use. The choice of species or variety with better yield potential is obviously important for economic reasons. However, the choice of species or variety is also important as a management strategy to offset acidification, as plants tolerant to soil acidity are more likely to be using water through better root growth and be reaching more NO_3^- deeper in the soil profile. The use of tolerant plants is important where subsoil acidity exists, particularly as the amelioration of acidity in the subsoil (i.e., below the soil volume where the lime has been incorporated) after liming is slow [39,85].

There is a risk, however, that reliance on crop choice alone, and not liming to correct acidity, will ultimately result in productivity losses as the soils acidify [84]. Reliance only on the use of acid-tolerant plants will be associated with the risk that acidification inputs will continue to some extent and, depending on the circumstances, this acidification may be hard to correct in the future. This situation often occurs in the high rainfall and nonarable pastoral areas in southern Aus-

tralia, where declines in pasture production are evident [86]. In these areas, there is a concern that with time there will be fewer pasture species with tolerance of acidity, particularly as the acidity develops at depth. An associated problem in these pastoral areas is the dependence on species such as subterranean clover that can persist at low pH, but their nodulation and growth may be adversely affected by the acidity [87]. Given the diversity of acidic soils, different acid-tolerant plants need to be identified and screened to ensure adaptation to the soil acidity complex. The issue should not be whether acidity tolerance is used but whether is it being used for the purpose of minimizing acid additions at the same time as increasing production.

The choice and balance of species and variety in the crop rotation are important, particularly in phase farming systems where a series of crops is alternated with a few years of pasture. The objectives of the rotations should include consideration of acidification influences such as water and NO_3^- use in the soil profile and soil and plant C dynamics. For example, wheat grown following a break crop such as canola or Indian mustard can extract more subsoil N than wheat grown following wheat [88]. This may be due to increased water uptake, possibly because the root system of the wheat crop was healthier because of lack of pathogens or other biological or physical changes associated with the break crop. The uptake efficiency of N (net uptake in whole tops at maturity per unit of N applied) does vary between wheat varieties and is thought to be a function of the size and activity of the root system [89]. Thus, differences in N uptake efficiency between genotypes may also be important in the recovery of N in field-grown crops. Usually it is necessary to include pulse crops in any long sequence of crops. It is well established that some pulse crops, for example, lupins, provide a strongly acidifying event in the rotation [2,48].

Market considerations as well as climate and soil characteristics mostly influence the design and management of rotation sequences. However, for the purpose of minimizing soil acidification, consideration should be given to the intensity of cropping and crop choice in the rotation for targeting high efficiency of nutrient removal and water use. The objective for sustainability is to manage the crop sequence so that the influence of strongly acidifying years is minimized. Particular attention should be paid to minimizing the effects of acid addition in the last pasture year in phase rotations or in pulse years in a continuous crop sequence. The choice of perennial species in the pasture phase is therefore preferred because of the greater opportunity to exploit the storage capacity of the deep subsoil [8]. Alfalfa is a useful plant for this purpose, although its sensitivity to acidity may limit this option. In the cropping sequence, consideration can also be given to regenerating the water storage capacity of the soil and ensuring that less acid is retained in the soil by careful management of N supply and efficient plant use of N.

5.4 Tillage, Stubble Management, and Organic Matter Dynamics

Organic matter is vital to the structural stability of soil, is an important reservoir of nutrients, and is essential for maintaining soil biodiversity. However, the addition of organic matter to soil can result in increases or decreases in soil pH, depending on the influence that the addition has on the balance of the various processes that consume and release protons. In the temperate crop–pasture systems of Australia, the levels of organic matter are built up with successive years of legume-based pasture (accompanied by N_2 fixation), often approaching a steady state in soil organic C that is dependent on rainfall and soil type [1,90]. Improving organic matter results in a significant increase in both the size and rate of the soil C and N cycles, both of which contribute residual acidity to the soil [4,52].

The introduction of cropping following pasture and accompanied by either a fallow phase or cultivation prior to crop establishment can lead to increased nitrification rates [91]. Crop residues also contain significant amounts of N as organic anions in the stubble (e.g., 14 to 22 kg N ha^{-1} [92,93]), which is lost to the atmosphere if this stubble is burned. Although stubble return is an obvious source of organic N for the soil, the organic content of the soil usually declines through cropping sequences irrespective of the crop used and method of tillage and stubble management [1,24,94,95]. For example, Slattery et al. [95] measured reductions in organic carbon in the 0 to 10 cm soil layer from about 15 to 11.5 g kg^{-1} over a period of 15 years with continuous cropping. Such losses of organic matter and associated declines in CEC significantly reduce the capacity of the soil to buffer against declines in soil pH.

The crop–pasture ley rotations in combination with fallow breaks, which were commonly practiced in southern Australia during the period 1960–1990, have been implicated in the widespread acidification throughout many regions [3]. The use of multiple cultivation has led to an exploitation of the accumulated organic matter and an increase in the rate of nutrient cycling. However, during the period 1990–2000 there was a significant change in the management of soil in preparation for cropping. The practice of burning stubble to make sowing operations possible has diminished as sowing equipment for handling stubble at sowing has been developed. Although stubble may still be burned for pest, weed, and disease management purposes, generally farmers prefer to return crop residues to the soil in crop rotations. This may involve a stubble retention system, where the plant material lost as litter during crop growth and the stubble from the previous crop is retained on the soil surface, or a stubble incorporation system, where the stubble is cultivated within a plow layer. Whatever the stubble management practice, it is necessary to reduce the quantities of stubble remaining prior to sowing (relative to that available at harvest) and there will still be some associated loss of organic material from the soil system. Farmers also prefer now to minimize the number of

times the soil is cultivated. Many farmers opt for direct drill (only soil disturbance during the sowing operation) or zero till that has virtually no soil disturbance. The return of plant materials to soil has important implications for managing soil acidification.

An alkaline effect results initially from the return of plant materials containing organic anions to the soil surface. This return of organic anions to the surface balances, in theory, the acidifying effects caused by the previous ammonification and nitrification of organic-N compounds, where at least 1 mole of protons was produced and retained in the soil. This balancing of acidifying and alkalizing processes was the likely outcome in the study reported by Poss et al. [12] where wheat as a rotation crop contributed little to acidification. The assumptions given for that study are that the stubble from the wheat crop has remained on the field and that any NO_3^- leached to depth in the soil has been taken up by root development. In such a crop year within a rotation, where only a few products escape the system, the acid additions should be mostly balanced with the organic anions as they are returned to the soil. In situations where there is more loss of crop residues and products from the system, residual acidity will remain in the soil. But practices such as stubble retention and minimum tillage would reduce and possibly balance this source of retained acid. However, in practice, these acid-producing and acid-consuming processes are spatially and temporally separated. The H^+ ion generating process of the soil and rhizosphere associated with the N cycle has occurred mostly deeper in the soil than at the soil surface or in the plow layer, where the OH^- ion generating processes as part of the return and accumulation of organic N occur. As a consequence, there is likely to be some stratification of acidification in the soil and, with time, development of permanent acidity [11].

It is recognized that acidification also results when carbon acids are formed from the organic anions as soil organic matter accumulates. The pasture component in the crop–pasture rotation is essential for increasing soil organic matter. The pasture phase in the rotation certainly contributes more acidity resulting from organic matter accumulation than crops. Heenan et al. [90] showed that the proportion of acid added from organic matter accumulation and product removal increased from 20 to 36% as the proportion of pasture in the rotation increased from 33 to 67%. Half to two-thirds of this was due to organic matter accumulation. Even though organic matter can have a strongly acidifying effect in crop rotations, any reduction in organic matter to counter this acidification will be counterproductive to the cropping system [11]. Maintaining organic matter in crop rotations is essential for the structural stability of soil, but it also has benefits that assist with countering acidity. The weakly acidic functional groups on soil organic molecules act as conjugate acid–base pairs and make soil organic matter an effective buffer for pH change [96]. Organic matter decomposition also releases organic acids known to complex toxic forms of Al [34]. The organic matter has a CEC originating mostly from carboxylate ($—COO^-$) groups, and this proportion of the soil

CEC is important for maintaining plant nutrients. Thus, the maintenance of soil organic matter is required in a highly producing crop rotation.

5.5 Product Removal

Soil acidification also results from the removal of products that contain organic anions (alkalinity), with unneutralized H^+ ions remaining in the soil. The amount of organic anions in products varies greatly. The removal of products low in organic anions, such as cereal grain, is less acidifying than removal of products high in organic anions such as alfalfa hay; for example, starch-dominated cereal grain removes 5 to 10 cmol($-$) kg^{-1} compared with removal with alfalfa hay of 100 to 150 cmol($-$) kg^{-1} [11]. Some acid addition to the soil must be accepted as part of a commercial farm operation. There is a limited opportunity to reduce this in a cropping system as the grain removal is unavoidable, but the losses in grain contribute little to acid input [2]. However, losses associated with the burning of stubble are avoidable.

Acidification associated with pasture–livestock or forage hay (export) enterprises can be more substantial. With grazing enterprises, practices such as feeding conserved forages on paddocks from which the forage was removed, returning dung and urine waste products to the donor field, and fencing to minimize camping behavior are recommended [11]. The intensity of grazing is also an important consideration as heavier grazing can result in greater amounts of N mineralization and the potential for either more plant N uptake or soil N accumulation [97].

6 REQUIREMENT FOR PRODUCTIVITY GROWTH

In the temperate agricultural regions in Australia, soil acidification is a form of land degradation associated with highly productive agricultural systems. Acidification has been recognized to date in the higher rainfall crop rotation areas associated with high input–high output cropping systems. In these areas awareness exists (mostly among primary producers) that acidification is a major problem. Here liming is seen as an economic option, despite the high cost of lime and freight [36,98]. In the medium rainfall areas, there is only limited awareness of acidification as a form of land degradation. In all these cropping areas, it is possible to restrict acidification by use of management practices that minimize acid accumulation and do not limit productivity growth. Within the overall goals and objectives of the farmers, the following strategies should be considered to meet nonacidifying outcomes.

Nonacidifying systems involve the efficient use of soil N and water. In phase farming systems, deep-rooted perennial species should be considered for creating soil water deficits and thereby less opportunities for drainage. Crop

choice, rotation choice, and soil management must be integrated so that the development of vigorous root systems is achieved. There should be more precision in the use of N fertilizer to ensure optimal crop N-use fertility. Wherever possible, plant materials should be returned to the soil at the site of origin. No-till systems should be used as this allows the intensification of crop sequences in the rotation with more opportunity for effective use of soil N. Liming the soil will often be undertaken in association with these nonacidifying management practices. Soil testing and the use of models for determining optimal lime and N fertilizer rates should be part of this practice.

Crop production in the medium to high rainfall areas in Australia has experienced an ongoing productivity growth of about 2.5 to 3% during the past few decades [99]. Soil acidification is a form of land degradation that can be accelerated in seeking more productivity growth. However, the nonacidifying strategies given previously are entirely consistent with best practice farm management for realizing further productivity growth. The emphasis in this chapter has been on a specific farming system in defined areas within Australia. However, the principles for the development of nonacidifying farming systems have a much wider application. The rapidly increasing population of the world is forcing food crop production onto more marginal acidic soils. It has been predicted that world population will increase between 2000 and 2050 from 6 billion to 10 billion, with a requirement to maintain or increase the growth rate in production [100]. The outcome of increased farm productivity must be established as a consequence of the functioning of the total interactive agricultural, environment, and social system and should be based on an understanding of the interrelationship between the soil and plant system.

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16

Managing Acidification and Acidity in Forest Soils

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1   INTRODUCTION

Acidification of forest soils is one of the major problems facing forestry throughout many regions in the world. The adverse properties brought about by acidification and encountered by trees are essentially the same as those faced by crop plants, i.e., low availability of base cations and high loading of Al on the soil cation exchange system [1]. However, the longevity of forest systems, where even in intensively managed plantations the rotation time may be in excess of 40 years and in more natural forests over 120 years, poses a number of specific problems. The aim of this chapter is not to discuss in depth the causes and effects of acidity on forest ecosystems, but rather to discuss the difficulties and implications of trying to manage soil acidity in forest soils.

2   CAUSES OF INCREASED ACIDITY IN FOREST SOILS

2.1   Naturally Occurring Acid Soils

Within any ecosystem soil acidification will occur when acidity-generating processes outweigh acidity-consuming processes [1]. In most nonmanaged ecosys-

tems, base cation depletion is balanced by (1) uptake into plant biomass, (2) leaching by vertical water flow, and (3) cation consumption and resupply by soil buffering and mineralization. In many temperate and tropical forest ecosystems, these processes have led to natural acidification of forest soils over a number of decades. In a review of calcium in terrestrial ecosystem processes [2], a number of examples of natural soil acidification have been described. In tropical forests, high soil acidity and Al toxicity are common [3]. In South American central lowlands, it was estimated that 43% of the land (350 million ha) is potential affected by Al toxicity (defined as >70% of the soil cation exchange capacity being occupied by Al). The high levels of soil acidity are a result of rapid decomposition of organic matter due to the high temperatures and high rainfall exceeding evaporation, leading to poor retention and leaching of base cations. In temperate spruce–fir forests of the eastern United States, precipitation in excess of evapotranspiration is thought to have produced highly acidified upper soil horizons. In these horizons, the pH is <3.2 and the base saturation less than 5% [4].

The high removal of base cations in tree biomass also leads to depletion of Ca and Mg in soils. Based on work of a number of authors [5–7], McLaughlin and Wimmer [2] describe a number of scenarios in which growth of forests leads to depletion of soil base cations. In an example of postglacial primary succession, the development of a forest community on base-rich, N-poor substrate results in increasingly high incorporation of base cations and N into the biomass and the soil organic matter. The nutrient storage in the organic matter helps to buffer against nutrient deficiencies. The system takes several hundred years to develop but results in more acidic forest soils with lower contents of base cations. The changes in soil Ca suggested by Ulrich [5] are supported by data on the removal of Ca from the soil in a 250-year-old primary succession sequence in Alaska [7]. After 250 years, 75% of the soil Ca was lost, but more significantly for managed forests, approximately 50% was lost after the first 100 years. McLaughlin and Wimmer [2] describe forest growth leading to three acidifying chemical processes:

1. Incorporation of Ca into woody biomass
2. Loss of Ca by increased leaching as H replaces Ca on cation exchange sites
3. Reduced availability of Ca due to Al antagonism

Van Breemen [8] suggested that soil development is strongly affected by tree vegetation type. Thus, growing forests are themselves a cause of soil acidity.

In temperate regions, managed forests are mostly replanted forests or remnants of natural postglacial forests. Replanted forests have often been established on nutrient-poor soils unsuitable for agricultural production. Similarly, remnant forests are often on soils too poor or too inaccessible to warrant clearing for agri-

culture. The initial poor soil conditions exacerbate the acidifying effects of forest growth.

2.2 Acid Deposition

In Europe and North America, acid precipitation has greatly increased rates of soil acidification in forest ecosystems. The increased soil acidity is a result of both direct proton input and internal proton production during nitrogen turnover. The acidification of forest soils has a number of consequences for the physiology of trees and the element budget of ecosystems, which must be considered if soil acidification is to be ameliorated by liming.

The common symptoms of tree damage are Ca deficiency in the eastern United States [9] and Mg deficiency in central European forests [10,11]. In an attempt to evaluate the changes in nutrient supply to vegetation, Robarge and Johnson [12] divided nutrient pools into capacity factors and intensity factors. Capacity factors are slow-reacting pools. In the case of base cations, capacity factors are weatherable minerals, organic matter, cation exchange capacity, and base saturation [2]. Intensity factors include short-term variations in ratios of base cation to Al and changes in strong anion concentrations in the soil solution, as well as changes in factors affecting mass flow of nutrients in the soil solution, such as transpiration, and additional factors removing nutrients from vegetation, i.e., foliar leaching.

Increased soil acidity in forests has resulted in increased leaching rates of base cations and increased availability of Al. Whereas in forests in the northeastern United States most emphasis has been placed on the increased depletion of Ca from soils [13,14], in European forests depletion of both Ca and Mg is of major significance [1]. Joslin et al. [14] estimated rates of leaching of Ca in forests affected by acid deposition to be approximately double the natural leaching rates. In the northeastern United States, a decrease in nutrient supply capacity has been happening for the last 60 years [9]. This is evident as a decreased cation exchange capacity of the humus layer and reduced retention and availability of Ca in the humus layer [15]. For a number of sites in Germany, Ulrich [1] reported a loss of nutrient cations and a decrease in base saturation. McLaughlin and Wimmer [2] suggested that changes in intensity factors appear to be the primary effect of acid deposition in forest soils, which have been subject to depletion of nutrient supply capacity. Ratios of base cation to Al are lower in the mineral soils that in organic upper soil horizons, resulting in limited growth of roots in the mineral soil. Low base cation/Al ratios affect the uptake of both Ca and Mg by tree roots [16] and also lead to injury to roots [16,17]. A number of studies have shown reduced root penetration into deeper soil layers, leading to shallower root systems on acid soils [4,18,19].

In addition to the changes that have taken place in forest soils because of proton inputs, anthropogenic inputs have led to nitrogen and heavy metal accu-

mulation in forest ecosystems [20]. Many forest ecosystems in both Europe and North America have reached nitrogen saturation [21,22]. Nitrogen saturation is the point at which N input rates exceed rates of aboveground and belowground utilization [23]. Eutrophication can have a number of negative effects on ecosystems, such as changes in vegetation cover. However, N saturation can also have significant effects on processes associated with acidification. Loss of N in the form of NO_3 can greatly increase cation depletion and mobilization of Al. In addition, in Europe, large areas of groundwater used for extraction of drinking water are under afforested areas [20].

3 LIMING FOREST SOILS

3.1 Liming Materials

In many countries in Europe, liming has been used as a method to counteract the effects of acid deposition [24–26]. Liming has been carried out with two primary aims, either to reverse soil acidification or to prevent further acidification (compensatory liming). In both cases, lime is applied to the surface humus layer. Only after trees have been cleared from the site is deep incorporation of lime into the soil possible. For compensatory liming, an amount of lime added is sufficient to neutralize the estimated proton input. For reversal of soil acidification, an amount of lime in excess of the estimated proton input is added. Most trials or liming measures have been carried out using calcite ($CaCO_3$) or dolomite [$CaMg(CO_3)_2$] mainly in a ground or half-sintered form (Table 1). For higher additions of Mg, kieserite ($MgSO_4$) has often been used. The rates of addition vary between 50 and 8000 kg ha^{-1} but most commonly between 2000 and 5000 kg ha^{-1}.

The buffering of protons by calcite and dolomite occurs in two steps [27]. Calcite

$$\text{Step 1: } CaCO_3 + H^+ \rightarrow HCO_3^- + Ca^{2+}$$
$$\underline{\text{Step 2: } HCO_3^- + H^+ \rightarrow CO_2 + H_2O}$$
$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

Dolomite

$$\text{Step 1: } CaMg(CO_3)_2 + 2H^+ \rightarrow 2HCO_3^- + Ca^{2+} + Mg^{2+}$$
$$\underline{\text{Step 2: } 2HCO_3^- + 2H^+ \rightarrow 2CO_2 + 2H_2O}$$
$$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O$$
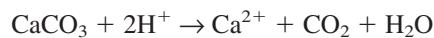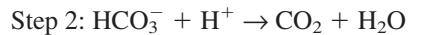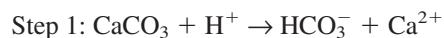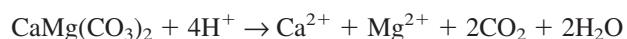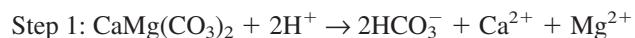
The two dissolution steps as shown in the preceding equations buffer at different pH ranges. The buffering range for the step 1 is pH 8 to 6.5, whereas for step 2 it is 7 to 4.5 [28]. The mobile buffer substance is HCO_3^-, which extends the deacidification front down the soil profile with the seepage water.

TABLE 1 Examples of Liming Trials Showing the Type and Amount of Liming Material Used and the Maximum Change in pH in the Soil Profile: Soil pH Values Before and After Liming

Site	Year	Liming material	Amount added (kg ha^{-1})	Effect	References
Fagne de Chimay, Belgium	1989	Calcite	50 to 8000	Increase of 0.16 pH units per t CaCO$_3$ ha^{-1} applied	31
Hils, Germany	1982	Calcite			32
Kahleberg, Germany	1985	Dolomite (50% CaCO$_3$, 30% MgCO$_3$)	7000	Increase in pH from 3.8 to 4.2	33
Prüm, Germany	1985	Dolomite liquid suspension	~3000	Increase in pH by 0.3 unit	34
Eggegebirge, Germany	1985	Calcite Dolomite (16% MgCO$_3$)	3000 3500	Increase in pH from 2.5 to 3.8	35
Grunewald, Germany	1986	Calcite/dolomite	6100	Increase in pH from 3.3 to 5.5	36
Höglwald, Germany	1984 to 1990	Dolomite	4000	Increase in pH from 3.8 to 6.4	27
Åseda, Sweden	1977	Calcite	5000	Increase in pH from 3.9 to 4.8	37
Farabol, Sweden	1976 to 1987	Calcite	500 per year	Increase in pH from 4.0 to 6.5	37
Fäxboda, Sweden	1980	Dolomite	412 Ca, 230 Mg	Increase in pH from 4.0 to 5.9	37
Norrliden, Sweden	1971	Calcite	5000	Increase in pH from 4.1 to 6.1	37
Several sites in Finland	1959 to 1962, relimed 1979 to 1982	Calcite	2000 4000	Increase in pH from 4.2 to 5.6	38
Susquehannock, Pennsylvania	1985	Dolomite (12% Mg)	2240	Increase in pH from 3.8 to 5.4	39

The rates of dissolution will depend upon both the liming material properties, such as the grain size, and the relative amounts of calcite and dolomite. In addition, the rate of dissolution will be affected by a large number of site factors, including

1. The acidity of the soil
2. Acid deposition
3. Soil temperature
4. CO_2 partial pressure of the soil air
5. Removal of the dissolution products with the seepage water

Except in soils with high porosity, lime particles are generally not translocated with the seepage water, and movement into deeper soil layers is dependent upon incorporation by earthworms [27].

3.2 Liming Trials

In Germany, liming was used in forests in the 1950s and 1960s to increase N turnover and change the humus from a mor to a mull type [24]. The objective of the treatments was to increase the biological activity in disturbed topsoil layers on acid soils and thereby release nutrients stored in the humus layer. This liming was often combined with P fertilization. From these trials, much can be learned about the long-term effects of lime application to the forest ecosystems. Details of many of these studies are given in Huettl and Zoettl [24]. Between 1953 and 1965, more than 100,000 ha of forestland was limed [29]. In 1983, Aldinger [30] investigated the effects of liming carried out in the 1960s and 1970s as a measure to counteract the effects of soil acidification. In these trials, ground limestone was applied at a rate of 2500 to 3000 kg ha^{-1}. In 50 limed *Picea abies* (Norway spruce) and *Abies alba* (silver fir) stands, which had shown symptoms of a new type of forest decline since the late 1970s, a positive effect of lime was found in that the pH of the humus layer was increased. The effect of liming on soil pH of a number of other sites is shown in Table 1. At all sites, lime application resulted in an increase in soil pH. Only small changes were shown at the Fagne de Chimay site, but the change in soil pH was estimated only 1 year after application [31]. There is, however, no clear relationship between the amount of lime applied and the change in pH.

As already discussed, the rate of dissolution of lime is dependent upon a number of factors. Kreutzer [27] estimated the rates of dissolution at 4000 kg ha^{-1} dolomite application at the Höglwald site and found complete dissolution 6 years after application, where the decrease in carbonate could be described by an exponential equation with a half-time of about 13 months. However, even when sufficient time for dissolution of lime had elapsed between application and sampling, it is noticeable that the changes in pH were primarily in the upper (organic) soil layer (Table 2). Because of the different soils sampled at these sites, soil depth in

TABLE 2 pH Changes in the Soil Profile After Liming for a Number of Liming Trials: Soil pH Values Before and After Liming

Site	Soil layer defined	pH change	Soil layer defined	pH change	References
Kahleberg, Germany	0 to 30 cm	3.7 to 4.3	30 to 60 cm	None	33
Eggegebirge, Germany	O horizon	2.5 to 3.8	A horizon	None	35
Grunewald, Germany	0 to 10 cm	3.3 to 4.1	>10 cm	None	36
Höglwald, Germany	Oh-layer	2.8 to 4.4	7 cm	None	27
Åseda, Sweden	Organic layer	4.0 to 4.8	0 to 10 cm	4.6 to 4.7	37
Farabol, Sweden	Organic layer	4.0 to 6.4	0 to 10 cm	4.2 to 4.7	37
Fåxboda Sweden	Organic layer	4.1 to 5.9	0 to 10 cm	4.6 to 4.8	37
Several sites in Finland	Upper humus	4.2 to 5.6	Eluvial layer	3.8 to 4.1	38
	Lower humus	3.4 to 4.9	Illuvial layer	None	
Susquehannock, Pennsylvania	0 to 5 cm	3.8 to 5.4	10 to 15	4.1 to 4.5	39

cm does not always represent a similar physical soil layer; however, a general trend can be seen in that pH changes below 10 to 15 cm are absent or small.

The longer term liming trials also allow estimation of the effects of liming on forest health over a time period in which effects could be expected. In the trials investigated by Aldinger [30], the pH of the humus layer was increased, but the most common symptom of forest decline, needle loss, was not reduced. Similarly, little improvement in tree health was found in limed and fertilized Black Forest stands [40] or in limed stands in northern Bavaria [41]. In their review of a large number of liming trials, Huettl and Zoettl [24] drew the conclusion that addition of $CaCO_3$ alone is insufficient to improve the nutrition, growth, or vitality of trees. In sites in the northern Black Forest investigated by Aldinger [30], it was shown in subsequent work [42] that a number of soil parameters, such as cation exchange capacity, base saturation, and exchangeable Ca (calcite application) and Mg (dolomite application), were increased. This change resulted in higher Ca contents in needles but lower levels of K in needles. The decrease in K concentration in needles was attributed to Ca inhibition of K uptake by the roots. Further, Huettl and Zoettl [24] suggested that this effect may not be unique to the K-poor soils of southern Germany. In an appraisal of 96 liming trials in Finland, Derome et al. [43] found that growth decreased by 3% in pine and 10% in spruce stands. Similarly, in Swedish liming trials, a decrease in growth was found in Scots pine and Norway spruce [44].

Thus, the conclusion is drawn that only lime materials that contain Mg will lead to revitalization of tree health [24]. In numerous studies, addition of Mg as either dolomite or highly available kieserite ($MgSO_4$) to trees showing decline symptoms rapidly resulted in a regreening of needles [24,45]. Addition of Mg-containing liming materials has increased growth and vitality of not only conifer-

ous stands in Germany [24,45] but also sugar maple (*Acer saccharum*) in the Allegheny plateau [39], with addition of dolomite in the latter also increasing the Ca and Mg contents of leaves by two and four times, respectively. This result probably reflected a strong improvement in soil conditions, i.e., an increase in exchangeable Ca and Mg, and a decrease in exchangeable Mn and Al. However, there was also a negative effect of a decrease in exchangeable soil K. The decrease in exchangeable soil K was also reflected in the leaves, where K levels decreased by approximately 30% but were presumably not sufficiently low to inhibit growth. Interestingly, *Prunus serotina* (black cherry) and *Fagus grandifolia* (American beech) did not respond to dolomite application. Clearly, the correct choice of materials for liming of forests depends upon the chemical status of the soils in addition to the pH.

Addition of Mg-containing liming materials or Mg fertilizers to Mg-deficient trees results in a rapid revitalization of the trees as long as the root systems are not irreversibly damaged by soil acidity. Whereas calcite application may have the positive effects of rapidly changing the pH of the soils, increasing exchangeable Ca, and decreasing exchangeable Al, the high levels of Ca may inhibit uptake of both Mg and K. Thus, the calcite application will not decrease Mg deficiency, the main symptom of forest decline, and may lead to induction of K deficiency. Hence, even in terms of base cation supply, the choice of liming materials must be carefully balanced against the site conditions.

4 CONSEQUENCES OF LIMING

4.1 Organic Matter Turnover and N Leaching

Many of the early liming trials carried out in the 1950s to 1960s were stopped when it became apparent that (1) growth was not improved and (2) a too rapid turnover of organic matter may lead to a release of NO_3 to groundwater [46]. In forest soils, the major proportion of soil N storage is in the organic layer. Liming is known to increase the CO_2 evolution from soil organic matter ([27] and references therein) and hence enhance turnover of the humus layer. However, the effect of liming on CO_2 evolution is influenced by a number of factors [27]:

1. Time
2. Soil temperature
3. Soil moisture
4. pH
5. Biological competition and synergism
6. Base-neutralizing capacity of the substrate

In addition, the C/N ratio of the humus material modifies the effect of liming. In soil samples from coniferous forest in Sweden, C/N ratios above 30 ini-

tially enhanced CO_2 evolution [47]. However, after this initial phase, CO_2 evolution was not enhanced but was even negatively affected, which was assumed to be due to N limitation after the easily decomposable matter had been respired. However, if the humus C/N ratio was between 24 and 28, the CO_2 evolution remained continuously enhanced compared with the unlimed treatment. Similarly, in four soil types (brown podzolic soil, humic gley, peaty-gley podzol, peaty-gley ranker), liming caused a net increase in N mineralization that decreased after an initial rapid phase [48]. The greatest decrease was found in the soils with the highest C/N ratios. In the Höglwald experiment [27], higher CO_2 evolution was maintained 2 years after liming, although the C/N ratio was between 28 and 30. This maintenance of higher CO_2 evolution was assumed to be due to atmospheric N deposition that prevented N deficiency. In subsequent years, the site of increased CO_2 evolution moved down the soil profile into the mineral soil as the deacidification front extended downward. The increase in CO_2 evolution was accompanied by a decrease in humus storage on the Höglwald site. The storage of surface humus decreased by 23%, approximately 7.2 t C ha^{-1}, over 6 years. A number of studies have shown that liming leads to a loss of C storage in the humus layer [25,29,36], but there are also a number of exceptions to this [49,50]. Marschner and Wilcynski [36] found a decrease in the C content of the forest floor from 27 to 17% in limed plots, corresponding to a humus loss of 15% in a pine plantation. In oak forests, after 20 months, organic C was reduced from 32 to 23% after liming with calcite [29]. In spruce–fir forest, losses of 80 t C ha^{-1} from the humus layer were determined, most of which represented redistribution into the mineral soil [36]. In contrast, at the Solling site, both increases and decreases in humus storage [50] or no effect [49] was found.

The decrease in the humus layer after liming has been attributed to increased microbial respiration [25,27]. However, Kreutzer [27] attributed loss of humus layer to other changes such as

1. Leaching of dissolved organic carbon (DOC)
2. Displacement of material rich in C in the mineral soil by the activity of earthworms
3. Redistribution of root mass

Following liming at the Höglwald site, the dissolved organic carbon leaching from the humus layer increased strongly, with a calculated flux of about 2 t C ha^{-1} over a 7-year period. Similarly, Marschner and Wilcynski [36] found an increase in water-soluble fulvic acids after liming.

The decrease of humus storage at the Höglwald site [27] resulted in 14% lower N storage on the limed plots and a dramatic increase in nitrate concentration in the seepage water under the rooting zone. The increase in NO_3 was not principally due to direct nitrification in the humus layer. Although the efflux of NO_3 was increased, the main component of the N efflux was organic nitrogen. At 40-cm

depth in the mineral soil, the main N efflux was NO_3, suggesting that the organic N was nitrified in the mineral soil. Emission of N_2O, an important greenhouse gas, was not increased by liming [27]. However, the N forms released after liming may be dependent on the liming materials used [25]. Liming of an acid mull humus or a moder humus with calcite or dolomite resulted in increased release of N primarily as NO_3, whereas after addition of gypsum, release of N was primarily as NH_4. The release of NH_4 into deeper soils layers and the production of NO_3 in deeper soil layers are not without consequences for soil acidity. Both can lead to an increase in soils acidity, and NO_3 will also lead to mobilization and transport of Al [2]; as a consequence, acidity is merely transferred to deeper soil horizons.

4.2   Retention or Release of Heavy Metals

Heavy metals from atmospheric pollution strongly accumulate in the humus layer of forest soils [51]. Liming at the Grunewald site [25] significantly increased the concentration of Zn, Cu, Cd, and Mn in the organic layer of the forest floor. This was attributed to a decrease in heavy metal solubility at higher pH and fixation of metals from throughfall and litter inputs. However, as a consequence of humus turnover, heavy metals may be released into the lower soil horizons [27]. Heavy metals, such as Cu and Fe, which form stable organic complexes, were shown to increase in the soil solution of a lime plot at Höglwald [27].

4.3   Fine Roots and Ectomycorrhizas

Acidification of forest soils leads to large changes in fine root distribution. In a spruce stand, soil acidity increased total fine root biomass but resulted in a much shallower root distribution [18,19] (Fig. 1). With increasing soil acidity, the specific root length (root length per unit dry weight) decreased; i.e., roots became thicker [19]. At the more acid sites of the Harz mountains and the Fichtelgebirge, higher total root biomass was found, but the roots were mainly confined to the organic layer and the 0–10 cm mineral soil layer. In contrast, at the Ebergötzen site, fine roots were found at a depth of 80 cm [19]. The differences in fine root distribution could clearly be related to Ca/Al ratios in the soil [19].

Revitalization of forest stands can be achieved only if the soil conditions are improved sufficiently to promote fine root development. In an investigation of the long-term effects of liming on root development at a number of stands in Sweden, liming with calcite had little effect on fine root biomass [52]. However, the specific root length increased with liming. The stands investigated varied in age (30 to 70 years), and between 5 and 18 years had passed between liming and investigation of the root density. All sites had shown a pH increase in the upper soil layers (see Swedish sites, Tables 1 and 2). A comparison of these results with those of earlier studies on the same sites [52] suggested that the effects of liming may decrease or disappear after 8 to 10 years.
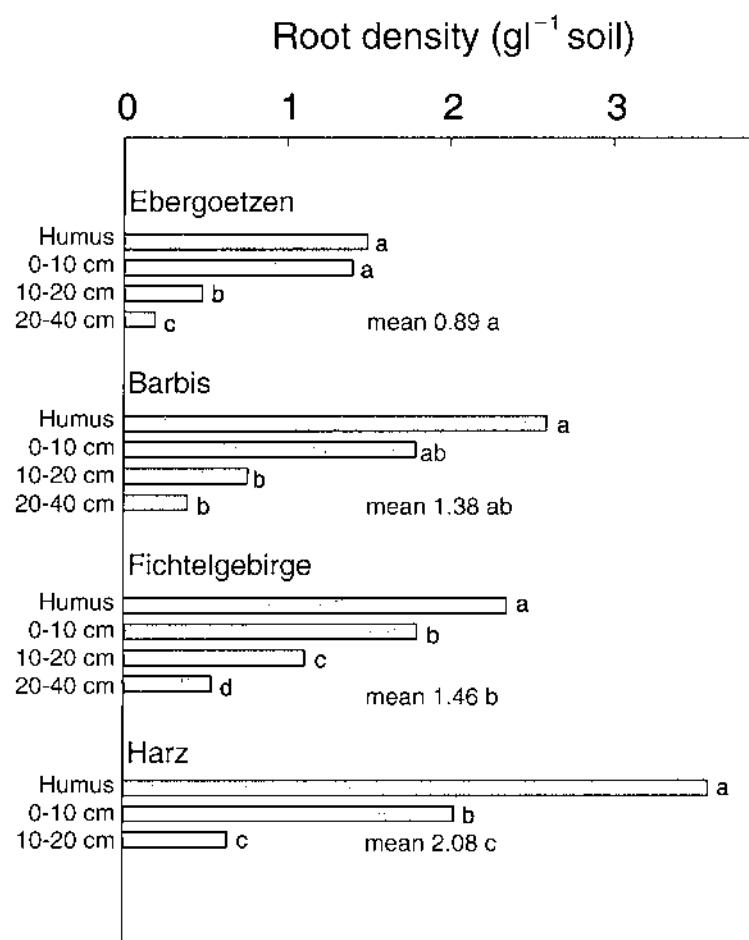
FIGURE 1 Fine root (<2 mm) biomass and distribution in four Norway spruce (*Picea abies*) stands growing on soils of differing soil acidity. Shown are the mean values for the soil horizon (0 to 40 or 0 to 20 cm). (Adapted from Ref. 19.)

There are a few examples in which liming substantially increased fine root density over the whole soil profile. Huettl and Zoettl [24] reported an increase in root growth in the mineral soil in a Norway spruce stand after addition of water-soluble Mg fertilizers. More significantly, surface liming led to increased shallowness of the root system due to growth proliferation in the limed humus layer (Fig. 2). Hahn [53] showed an increase in the root density in the humus layer 7
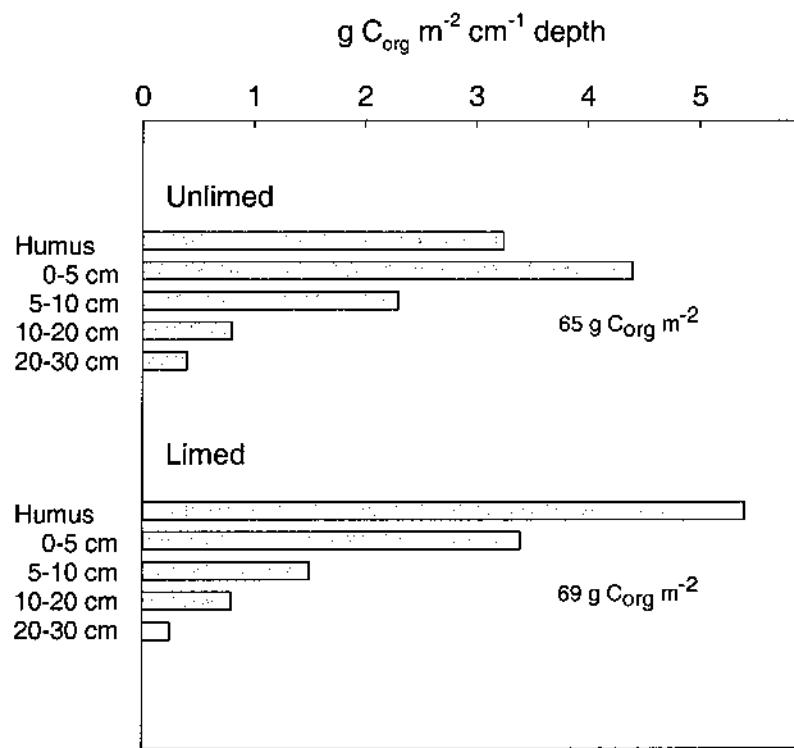
FIGURE 2 Distribution of fine roots (<1.5 mm) on limed and unlimed plots at the Höglwald site in 1991–1992. The site is an 80-year-old Norway spruce (*Picea abies*) stand. The limed treatment was limed in 1984 with 4000 kg ha^{-1} dolomitic lime (Ca/Mg ratio 1.1:1). Shown are the mean values for the soil horizon 0 to 30 cm. (Adapted from Ref. 27, original source Ref. 53.)

years after liming. There was no significant change in the total root density of the whole soil profile, and the increase in the root density in the surface humus appeared to be at the expense of the root density in the upper mineral soil; however, this should be interpreted with caution. Such increases in the fine root density in the humus layer after liming are not uncommon. Murach and Schünemann [54] found increased root growth in the humus layer of a Norway spruce stand after liming. Similarly, in a Norway spruce stand limed with dolomite in the Fichtelgebirge, the same effect was found [55]. An increase in the growth of roots in the surface humus was also found in the Swedish sites [53], but there were clear differences between sites, suggesting that liming may not automatically lead to shallower root growth.

The method used to apply lime may prevent surface growth of roots. Application of a liquid dolomite suspension greatly increased root growth in the 10- to 15-cm-deep mineral soil in a young Norway spruce stand [34]. There may also be considerable site and tree species differences in response to surface lime application. However, although there is no firm evidence that increased surface rooting has negative consequences, surface rooting may be undesirable under drought or high windthrow conditions.

Ectomycorrhizas play an important role in the mineral nutrition of trees [56]. Much of the information about the effects of liming on ectomycorrhizas has been gained from studies on sporocarps [57]. However, with the development of molecular identification techniques, it has been shown that aboveground sporocarp-based estimates of fungal diversity correlate poorly with belowground fungal diversity based on root colonization [58]. Based on sporocarp estimations, liming decreased the number of ectomycorrhizal species that produced sporocarps [57,59] and increased the number of saprophytic species producing sporocarps [59]. In investigations using either morphological or molecular identification of ectomycorrhizal fungi on roots, again clear changes in community structure were found [27,58,59]. Although it is well known that the physiological benefits of ectomycorrhizas to trees differ between ectomycorrhiza species [56], the significance of the change in community structure cannot be estimated at present. It is known that ectomycorrhizal community structure is altered by soil acidification [60,61]; however, it is unclear whether the changes induced by liming are a reverse of the acidification affects.

5   FOREST MANAGEMENT

Liming of forest is often carried out after cutting. However, forest harvesting, in particular clear felling, has been shown to decrease humus storage [62] and to increase rates of NO_3 runoff [62,63]. The decreased humus storage may be due to an increase in microbial degradation because of increased soil temperatures on clearfell sites. In an assessment of a number of catchments from clearfelled spruce forests, NO_3 was the main strong acid anion produced that led to Al release [63]. In acid beech forests, removal of trees to form forest gaps (30 m in diameter) resulted in a significant decrease in pH at 15 cm soil depth and a significant release of NO_3 with the seepage water (80-cm soil depth) [64]. Concentrations of NO_3 in the seepage water were between 10 and 18 mg L^{-1} and caused a strong release of Al. The release of NO_3 was suggested to be due to decreased root uptake in the gaps, causing a strong disruption of the N cycle. Liming of the gap with 3 t ha^{-1} of fine dolomite strongly reduced the amount of NO_3 released with the seepage water. This was suggested to be due to stimulation of growth of herbaceous vegetation after liming, the roots of the vegetation compensating for the lack of NO_3 uptake by tree roots. The small size of the gaps prevented significant soil warming. In further work

[65], in a comparison of the effects of liming on the gaps and the surrounding beech stand, microbial biomass increased in the limed stand but decreased in the limed gap. This was suggested to be due to a decrease in the amount of ectomycorrhizal hyphae in the soil of the limed gap. Emission of N_2O was six times higher at the nonrooted center of the gap than at the rooted edge [66].

As discussed earlier, forest growth may lead to removal of base cations from the soil into tree biomass. Subsequently, tree harvesting may lead to removal of base cations and an increase in the potential for soil acidification. The removal of base cations can be strongly influenced by the harvesting method used [2]. Although the foliage and branches are only 20 to 30% of the biomass of the boles, these parts have much higher nutrient concentrations. As a consequence, there are considerable differences in nutrient removal using whole-tree and bole-only harvesting methods. For Ca, whole-tree harvesting results in two- to three-fold higher removal than bole-only harvesting [13]. Leaving residues on site to mineralize after sawlog harvesting can also greatly replenish Ca in the soil [67]. Fifteen years after harvesting of a deciduous forest in the eastern United States, it was estimated that whole-tree harvesting led to a net loss of Ca of 478 kg ha^{-1}, whereas sawlog harvesting resulted in a net gain of 56 kg Ca ha^{-1} [2,67]. In beech and spruce forest in Germany, branch removal compared with bole-only removal increased base cation losses by 20% in beech and 100% in spruce [6].

The preceding calculations show that forest-harvesting methods can alter the removal of base cations. However, many of the forest ecosystems in Europe and North America are subjected to high loads of N due to high atmospheric inputs [21,22]. To protect groundwater from excessive NO_3 loads after harvesting, a number of harvesting methods have been suggested [22]. However, these are in part the opposite of recommendations to prevent removal of base cations. For, example it has been shown that whole-tree harvesting can greatly limit N losses for the first years after harvesting [22]. Removal of slash not only prevents leaching of N from the slash materials but also promotes rapid regeneration of vegetation cover [68]. Limitation of N losses by liming was also shown in beech forest gaps, which was again attributed to a strong growth and nutrient sink function of the ground flora [66]. In the spruce forest of the Höglwald, although liming stimulated the growth of the ground flora, the nutrient sink function of the shade-tolerant vegetation was insufficient to prevent N losses [69]. This finding suggests that liming to ameliorate soil acidification should best be carried out when the canopy has been opened to improve light conditions. The size of opening in the canopy must be balanced to prevent strong losses of humus storage and hence N due to large changes in micrometeorology. Thus, large-scale clear-cutting and liming before stand reestablishment may not be an appropriate strategy for management of acid forest soils. Rather, soil amelioration should be carried out in small area cuts. Such considerations are particularly important in the restructuring of coniferous plantation forests currently taking place in much of Europe.

6   CONCLUSIONS

It is apparent that the changes brought about by pollution in forest ecosystems can rarely be rectified simply by liming. As is almost always the case, not one single stress factor, in this case acidity, is acting on forest ecosystems. Rather, over a number of years, forests have had to suffer the buildup of a number of stress factors. Hence, a monocausal solution (liming) may have the desired ameliorating effect but may also be the cause of a number of other negative effects. Thus, although liming is the only rapid means of increasing soil pH, it must be considered within the framework of an integrated management system using both chemical amelioration and silvicultural measures.

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Role of pH in Phytoremediation of Contaminated Soils

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1 INTRODUCTION

Soil contamination by heavy metals, radionuclides, and organic compounds poses significant health risks to humans and animals as well as agricultural production. Contamination of soils has resulted from industrial activities such as mining and smelting, the development of the nuclear industry, the disposal of municipal wastes and sewage enriched with metals, and the use of certain pesticides [1–4]. The remediation of contaminated soils represents a significant expense to many industries and governmental agencies. Soil contamination by toxic metals and radionuclides can be found in almost any country in the world. Because of the large areas of contaminated soils, engineering-based remediation methods, such as excavation, become economically impossible for most of the contaminated sites.

Phytoremediation, the use of plants to remediate contaminated soils, sediments, and waters, has emerged as a cost-effective and environmentally sound alternative for the cleanup of contaminated soils and waters [4–7]. Since the con-

cept of phytoremediation was proposed by Chaney [8], there has been increasing interest in developing phytoremediation technology for the cleanup of contaminated soils [4,9–11]. Phytoremediation of contaminated soils has two major strategies: phytostabilization and phytoextraction. Phytostabilization is the use of plants and soil amendments for physical stabilization of the soil to minimize the migration of contaminants and to induce the formation of insoluble contaminant species that would reduce contaminant bioavailability in the contaminated soil [4,12]. Phytoextraction is the use of plants to remove contaminants from the soils. With the continued cultivation and harvesting of selected plant species at the contaminated sites, the soil becomes decontaminated [5,11,13].

The success of using plants to extract contaminants from soils depends on the bioavailability of the soil contaminants to plant roots and the efficiency of contaminant uptake, translocation, and accumulation by the plants. Soil pH is an important factor affecting adsorption and desorption of contaminants in soils, the availability of contaminants to plant roots, and the transport of contaminants into root cells. This chapter focuses on phytoremediation of soils contaminated by toxic metals and radionuclides and the role of altering soil pH in phytoremediation. For phytoremediation of organic contaminated soils, readers are referred to other publications [14,15].

2   ADSORPTION AND DESORPTION OF CONTAMINANTS IN SOILS

Metal solubility in soils is strongly influenced by soil pH and soil characteristics [16–18]. The main processes associated with the adsorption and desorption of metals in soils are weathering, dissolution and solubility, precipitation, uptake by plants, immobilization by soil organisms, exchange on soil exchange sites, specific adsorption and chemisorption, chelation, and leaching [19]. Most metals are relatively more mobile under acid and oxidizing conditions and are strongly retained under alkaline and reducing conditions [20]. For example, Pb, Zn, Cd, Cu, Co, and Hg are more soluble at pH 4–5 than in a pH range of 5–7 [21]. However, As, Se, and Mo are less soluble under acidic conditions because of the anionic forms of these contaminants.

2.1   Adsorption of Contaminants in Soils

Soil pH can significantly affect the adsorption of heavy metals in soils [17,22,23]. Adsorption of Pb, Cd, Cu, Ni, and Zn by soils was closely correlated with soil solution pH, and increasing solution pH increased metal adsorption [16,24,25]. A linear correlation between Pb and Cd distribution constants and soil pH and organic matter was found for 33 temperate soils [26]. The relationship between metal adsorption and equilibrium soil solution pH was dependent on the initial

metal concentration. At low initial metal concentration, the adsorption of Pb, Cd, Cu, Ni, and Zn was independent of soil solution pH [24]. At high initial concentration, the adsorption of these metals increased when the soil solution pH was increased. The adsorption of As, an anionic contaminant, by soil clay minerals was highest at pH 5 and decreased significantly between pH 7 and 9 [27]. In a comparison of various soil properties (pH, cation exchange capacity, clay content, organic mater, and hydrous Fe and Mn oxide contents), Anderson and Christensen [28] demonstrated that soil pH was the most critical factor affecting the adsorption of Cd, Ni, Zn, and Co in the soils.

2.2 Desorption of Contaminants in Soils

Desorption of Zn, Cu, and Ni from metal-contaminated soils and sludge mixtures increased significantly with decreasing soil pH [29,30]. For each metal, there is a threshold pH value. Above this value, desorption of the metal is little affected by a further increase of soil pH [29,30]. The threshold pH values are 6.3 for Ni, 5.8 for Zn, and 4.5–5.5 for Cu [29,30]. The accumulation of Zn, Cu, and Ni in ryegrass responded to soil pH in a pattern similar to the metal desorption from the soil to the soil solution [29].

In studying the effect of acidification and chelating agents on the solubilization of uranium (U) from contaminated soils, Ebbs et al. [31,32] found that maximum U solubilization was reached in the soil pH range 4–5. The increase of U desorption was coupled with low pH and the presence of chelating agent (citric acid) [32,33]. Citric acid is unique in enhancing soil U desorption because in its free acid form, it is capable of both acidifying the U-contaminated soil and complexing the U in the soil solution. Such reaction would drive U desorption from soil to soil solution [31–33]. In the absence of citric acid, lowering the soil pH by adding elemental S or an inorganic acid such as sulfuric acid or nitric acid had little effect on U desorption from the soil to the soil solution [31–33].

Desorption of As (an anionic contaminant) is increased with increasing soil pH. For example, the soluble arsenic concentration increased 10-fold following liming of As-contaminated soil [34]. Unfortunately, the increased As desorption from soils increases the risk of As contamination of surface water and groundwater in the areas with elevated As levels in the soil.

3 PHYTOSTABILIZATION OF CONTAMINATED SOILS

Phytostabilization is the use of plants and soil amendments to stabilize the soil physically (thus minimizing the migration of contaminants) and to induce the formation of insoluble contaminant species (thus reducing contaminant bioavailability in the contaminated soil) [4,12,35]. Phytostabilization does not remove the contaminants from the soil but inactivates the contaminants in situ. This

form of remediation may be appropriate for certain sites where a short-term risk-reducing practice is acceptable until final remediation of the site can be accomplished [12].

In phytostabilization, soil amendments are applied to contaminated soil; the site is then planted with selected plant species. The plants used in phytostabilization must be effective in contaminant accumulation in roots but less effective in the translocation of the contaminants from roots to shoots [12,35]. The soil amendments for phytostabilization should inactivate contaminants rapidly following application, preventing leaching and minimizing contaminant accumulation in plants. The most promising soil amendments for phytostabilization include alkalizing agents, phosphates, mineral oxides, organic mater, and biosolids [4,35]. Common alkalizing amendments are liming agents that have been used to increase soil pH of sludge-amended soils and acid mine spoils to inactivate metal contaminants [12,36]. Liming has to be done periodically to maintain a desired soil pH at which metal contaminants are insoluble.

Phytostabilization has been demonstrated for Pb-contaminated soils [37,38]. After application of P (0.5% of soil weight) or Fe oxyhydroxides (10% of soil weight) to a Pb-contaminated soil, there was a significant shift of the Pb fraction, mostly from the soluble Pb fraction to a nonsoluble fraction [38]. The soil amendments producing such a shift in Pb sequential extraction reduced Pb accumulation in plant shoots by more than 90% [35,39]. Furthermore, Pb bioavailability, estimated by an in vitro simulated mammalian digestive assay [40], was reduced by more than 45% in Pb-contaminated soils after phytostabilization [35]. Growing *Agrostis capillaris* in Pb- and Zn-contaminated mine wastes, Cotter-Howells and Caporn [41] observed the formation of pyromorphite (Pb-phosphate minerals) from soil Pb and phosphate, demonstrating the role of certain plants in reducing Pb bioavailability. Phosphate amendments (phosphoric acid, phosphate fertilizers, or by-products high in P) are effective in inducing the formation of insoluble forms of Pb [37,42]. Application of P to Pb-contaminated soils produces pyromorphites that are insoluble even under strong acid conditions [43,44].

During the process of phytostabilization, the dense root systems play an important role in stabilizing the soil and preventing erosion by wind and rain [12,45]. Plants also help to minimize water percolation through the soil profile, thus reducing contaminant leaching. Plant roots can also provide surfaces for sorption or precipitation of contaminants [12]. The main advantage of phytostabilization is that it is easy to implement with low operating costs. Phytostabilization can be adapted to a range of site conditions and remediation needs. However, because phytostabilization does not remove contaminants from the soil, continuous monitoring of the site is needed during and after the process. To remove the contaminants from the soil without removal of the soil itself, phytoextraction technology can be used.

4   PHYTOEXTRACTION OF CONTAMINANTS FROM SOILS

4.1   Metal Speciation and Bioavailability to Plants

Depending on the chemical nature of the metals and soil properties, metals in soils occur in various forms (soluble, exchangeable, complexed, organically bound, oxide, and solid particulate). Two examples are As and Pb. Arsenic is present in most contaminated soils either as As_2O_3 or as arsenic compounds derived from As_2O_3. Arsenic may also be present in organometallic forms, such as methylarsenic, $H_2As_2O_3CH_3$, and dimethylarsenic acid, $(CH_3)_2As_2O_3H$, which are active ingredients in many pesticides. Two main redox states, As(III) and As(V), have been found in soils. Arsenic (III) is generally considered more mobile and toxic than As (V) [46]. The forms of Pb can be ionic, oxides, hydroxides, and lead–metal oxyanion complexes. Lead forms both mononuclear and polynuclear oxides and the corresponding hydrates and hydroxides. Lead and Pb-hydroxyl complexes are the most stable species under most soil conditions. These forms of Pb are not readily available to plants. Lead also forms stable complexes with both inorganic (e.g., Cl^-, $CO2_3^-$) and organic ligands (e.g., humic and fulvic acid) in soils. Soluble Pb also reacts with carbonates, sulfides, sulfates, and phosphates to form low-solubility compounds, thus reducing availability to plants [47].

Soil pH is one of the most important factors controlling metal solubility in soils; therefore, soil pH can significantly affect metal availability to plants. The pH interacting with soluble organic matter also affects metal solubility. In soil with a high organic matter content and a pH of 6 to 8, Pb may form insoluble organic Pb complexes. If the soil has low organic matter at the same pH, hydrous Pb-oxide complexes or Pb-carbonate or Pb-phosphate precipitates may form; these Pb forms are not easily absorbed by plant roots [46]. At pH 4–6, the organic-Pb complexes become more soluble and hence may become available to plant roots [46].

The change of soil pH in the rhizosphere because of the release of proton and organic acids from plant roots could significantly affect metal bioavailability to plants. The rhizosphere pH change is often caused by an imbalance in uptake by roots of cations and anions, CO_2 respiration, excretion of organic acids from roots, and microbial activity [48,49]. A classic example of root-induced rhizosphere pH change is the plant response to Fe deficiency, whereby roots release protons and or phytosiderophores to the rhizosphere [49–51].

Using a pea (*Pisum sativum*) mutant E107, an Fe hyperaccumulator resulting from increased activity of ferric reductase in roots [52], we found that the Fe deficiency–induced increase of ferric reductase activity was strongly regulated by the pH (unpublished results). At pH 6.0 or below, reductase activity was significantly higher than at pH 6.5 or above. Not only did the accumulation of Fe increase, but there were significant increases in accumulation of other metals such

as Al, Cu, Mn, Pb, and Zn in this mutant even at relatively low levels (0.1–20 μM) of these metals in the solution (unpublished results).

4.2   Uptake of Contaminants by Roots

Several metal contaminants are also essential plant nutrients (Zn, Cu, Ni, and Mn), and others are not known essential elements for plants (Pb, Cd, U, Hg, and ^{137}Cs). Most metals enter root cells primarily through particular transport systems such as carriers or ion channels. The driving force for metal uptake by roots is the electrochemical potential established by the plasma membrane adenosine triphosphatase (ATPase) [53]. Root cells have a plasma membrane potential ranging from -100 to -200 mV [54,55]. This large electrochemical potential gradient across the root cell plasma membrane drives metals into root cells. Furthermore, the activities of these contaminants in the cytoplasm of root cells must be maintained at very low levels because of the pH and other chemical characteristics of cytoplasm. The lower intracellular activity coupled with a large negative membrane potential become a strong driving force for the influx of these contaminants into root cells.

The plasma membrane divalent-cation channels, which pass cations including Co and Ca [56–58], could be the transport pathways for certain metal contaminants into the root cells. There are experimental data suggesting that Zn, Cu, and Ni are transported into root cells via a common transport pathway [59,60]. Using radioactive tracers, researchers have studied voltage-gated cation channels in the plasma membrane of root cells and identified voltage-dependent Ca channels operating in the root cell plasma membrane [61,62]. Using isolated root cell plasma membrane vesicles, Huang and Cunningham [63] found that Pb could significantly inhibit voltage-dependent Ca channels. The inhibition of the Ca channel activity could result from blockage of the channel by Pb or competition between Pb and Ca for the transport pathway. The results are similar to those found in animal systems where Pb is transported into cells via the Ca channel [64]. If ion channels or ion specific transport systems are the pathways for the transport of these contaminated metals, alteration of the ion channels or transport systems through mutation could alter the specificity of contaminant transport and result in a substantially large amount of metals transported into root cells. Using isolated *Arabidopsis* Pb-accumulating mutants, Chen et al. [65] demonstrated that Pb-accumulating mutants also accumulated high level of Al, Ca, Cu, Fe, Mg, Mn, Ni, and Zn. The results are similar to those for the Mn-accumulating *Arabidopsis* mutant and pea bronze mutant [66–68].

4.3   Translocation of Contaminants from Roots to Shoots

For practical reasons, the contaminant concentration in plant shoots is the most important parameter for phytoextraction because the harvested portions of plants

at most contaminated sites are limited to the aboveground parts [13,69]. Most metals are rapidly absorbed by roots; translocation of the absorbed metals to shoots, however, is the limiting step for metal accumulation in shoots. Metal contaminants can be divided into two groups on the basis of their chemical properties [70]. Group 1 includes Ag, Cr, Hg, and Pb, which can be absorbed into roots but not easily translocated from roots to shoots. Group 2 includes Cd, Co, Cu, Mn, Mo, Se, and Zn, which are readily absorbed by roots and translocated to shoots. Plants, however, have mechanisms that limit metal translocation even for metals in group 2 because the photosynthetic apparatus of leaves is sensitive to excessive levels of metals.

In response to excess Cd, Zn, Cu, and Pb, plants produce phytochelatins to complex these metals, thus reducing their phytotoxicity [71]. Using two *Arabidopsis* mutants—*cad1-3,* defective in PC synthase, and *cad2-1,* deficient in γ-glutamylcysteine synthetase activity, Chen et al. [72] studied the response of these mutants to Pb exposure. Compared with the wild type, the Pb concentration in shoots of the two mutants was three fold higher, suggesting that in the wild type Pb is retained in roots by phytochelatins to avoid Pb toxicity in shoots.

There are a number of physiological processes involved in contaminant translocation from roots to shoots. These factors are contaminant unloading into root xylem, long-distance transport within the xylem to the shoots, and contaminant reabsorption from the xylem sap by leaf mesophyll cells. The general model for metals unloading into the xylem vessels involves the absorption of metals from soil solution into the root symplasm and then unloading of the absorbed metals from the xylem parenchyma into mature xylem vessels [59]. For most contaminants, the rate of translocation to shoots is much lower than the rate of absorption of these contaminants. For example, using the shoot-to-root concentration ratio to estimate Pb translocation to shoots, Huang and Cunningham [63] found that for any specific time period, the rate of Pb translocation to shoots is less than 30% of the rate of Pb absorption by the roots. Why is contaminant translocation from roots to shoots generally lower? Of the contaminants pertinent to phytoremediation, most are divalent cations. Once the contaminants are transported into the root cells, they are either precipitated in the cell or chelated with organic compounds. For long-distance transport, the contaminants have to be chelated with chelating compounds available inside the root cells. There are experimental data demonstrating that when synthetic chelates were added to nutrient solution, Pb translocation from roots to shoots increased rapidly [73]. The solution pH was critical in chelate-enhanced Pb translocation. When the solution pH decreased from 5.5 to 3.5, chelate-enhanced Pb translocation from roots to shoots increased 20-fold [73]. Metal accumulation in shoots is critical to the success of phytoextraction. In addition to identifying the hyperaccumulating variant and selection of mutants, use of soil amendments such as chelating compounds to solubilize and chelate metals has been shown to enhance translocation of metals to shoots [69,73,74].

4.4   Plant Species Variation in Metal Accumulation

Plant species vary significantly in metal absorption and translocation. A small number of plant species endemic to metalliferous soils can tolerate and/or accumulate high levels of toxic metals. These plants are called hyperaccumulators if they can accumulate more than 1000 mg kg^{-1} of Pb, Co, or Cr or more than 10,000 mg kg^{-1} of Zn, Mn, or Ni in plant shoots when grown in their natural habitat [75–77]. Accumulation of Zn in *Thlaspi* varies between 10,000 and 43,000 mg kg^{-1}. The copper concentration in *Haumaniastrum rosulatum* shoots is about 1000 mg kg^{-1}, whereas in *H. katangense* tissue it is as high as 8400 mg Cu kg^{-1} [77]. An As hyperaccumulator was identified from fern species [78]. This fern species can accumulate as much as 15,000 mg As kg^{-1} in the aboveground plant tissue. We compared As accumulation by this fern with a number of different fern species that have a similar growth rate and biomass accumulation and found that the arsenic concentration in this hyperaccumulating fern was approximate 200-fold higher than that of other plant species tested (unpublished results).

To date, there are approximately 400 known metal hyperaccumulators in the world [79]. Some of these metal hyperaccumulators have been tested for phytoextraction of metals from contaminated soils and sludges [10,80,81]. Field studies with Zn, Ni, and Cd hyperaccumulators *(T. caerulescens, Alyssum murale, A. lesbiacum, A. tenium)* demonstrated that these plant species accumulated high levels of Zn and Cd in the shoots [10]. The remediation potential, however, may be limited by these metal hyperaccumulators because of the slow growth rate and lower biomass production. Further studies with *T. caerulescens* and *Silene vulgaris* to remediate Zn- and Cd-contaminated soils have demonstrated similar results [80].

In the last 5 years, there has been increased interest in searching for metal-hyperaccumulating plants capable of producing high biomass [15,63,73,82]. Recent data demonstrate that metal hyperaccumulation can be achieved with selected high-biomass agronomic crops in conjunction with the application of soil amendments to the contaminated soils (see discussion later in this chapter).

In addition to the interspecific variation, intraspecific variation also exists. For example, Chen et al. [65] studied Pb transport in 74 *Arabidopsis* ecotypes and detected significant variation among ecotypes in the tolerance and accumulation of Pb. The tolerance index (TI), defined as the ratio of root length for plants grown on the agar medium with Pb (16 mg kg^{-1}) to root length on control medium (no added Pb), ranged from 0.17 to 1.2 [65]. The shoot Pb concentration among 74 *Arabidopsis* ecotypes varied from 80 to 800 mg kg^{-1}. The results demonstrate significant intraspecific variations in Pb accumulation by these *Arabidopsis* ecotypes. Identifying plant species with high efficiency for targeted metal accumulation will further reduce phytoextraction costs and accelerate soil cleanup processes.

5   METHODS OF ENHANCED METAL PHYTOEXTRACTION

5.1   Soil Amendments Enhance Metal Accumulation

Plants grown on contaminated soils generally do not accumulate very high concentrations of the targeted contaminants in the aboveground plant parts except for metal hyperaccumulators, such as Zn or Ni hyperaccumulators, as discussed earlier. Most current metal hyperaccumulators have limitations in commercial phytoextraction because of the slow growth and low biomass production by these plants. Extensive research has been conducted in various laboratories to induce metal hyperaccumulation in non–metal-hyperaccumulating plants with high biomass production. With the application of various soil amendments to the contaminated soils, it is now possible to achieve the targeted metal concentrations for commercial phytoextraction [33,69,73,80]. The application of soil amendments could adjust soil pH, increase metal desorption from soil to soil solution, supply the chelating agents to buffer metal activity in the soil solution, and increase the metal translocation from roots to shoots.

Two major limitations of phytoextraction of contaminants from soil are the low metal availability in the soil and the inefficient translocation of the contaminants from roots to shoots. Most contaminants are rapidly accumulated in roots if the contaminants are bioavailable in the plant growth media; however, only a small portion of the absorbed contaminants is translocated from roots to shoots [69,81–83]. The success of phytoextraction becomes dependent on the increase and maintenance of contaminants concentrations in the soil solution and the enhanced translocation of contaminants from roots to shoots. Chelates and other chemical compounds have been used to increase the solubility of metals in plant growth media and could significantly increase metal accumulation in plant [18,36,84,85]. Data from a number of laboratories have demonstrated that chelates, organic acids, and certain chemical compounds can be used to trigger metal hyperaccumulation in several agronomic crops with high biomass production [32,33,69,73].

5.2   Phytoextraction of Lead, Uranium, Cesium 137, and Arsenic

For effective phytoextraction of contaminants from soils, each contaminant has to be considered separately because of its unique solution and soil chemistry and its transport characteristics in plants. In the following sections, we discuss the phytoextraction of Pb, U, ^{137}Cs, and As from contaminated soils and review the current progress in soil amendment–induced hyperaccumulation of these contaminants in selected plant species.

5.2.1   Lead

Lead contamination of soils resulted from industrial and mining activities; the use of Pb in paints, gasoline, explosives, and antispark linings; and the disposal of mu-

nicipal sewage sludges enriched in Pb [1–3]. Lead is considered one of the most frequently encountered heavy metals of environmental concern and is the subject of extensive remediation research [15,39,69]. The remediation of Pb-contaminated soils represents a significant expense to many industries and government agencies [4,15]. There are no reliable reports of plants capable of naturally hyperaccumulating Pb in significantly high concentration. Results from hydroponic and sand culture demonstrated that Pb accumulation in plants increased dramatically as soluble Pb levels in the plant growth media increased [63,82]. However, for most Pb-contaminated soils, Pb in soil solution is usually less than 0.1% of total soil Pb [69].

Early studies have indicated that application of chelates to soils increased Pb accumulation in plants [86,87]. These studies have led to the exploration of using soil amendments to enhance Pb desorption from soil to soil solution and Pb accumulation in plants. As an example, application of a synthetic chelate, N-(2-hydroxyethyl) ethylenediamine-triacetic acid (HEDTA) to a Pb-contaminated soil (total soil Pb 2500 mg kg^{-1}) resulted in a surge of Pb concentrations in shoots of corn and pea (Fig. 1). Shoot Pb concentrations for both species increased from less than 100 mg kg^{-1} for the control (no HEDTA addition) to more than 10,000 mg kg^{-1} for the HEDTA treatment (Fig. 1).

The increase of Pb concentration in plants is positively correlated with the
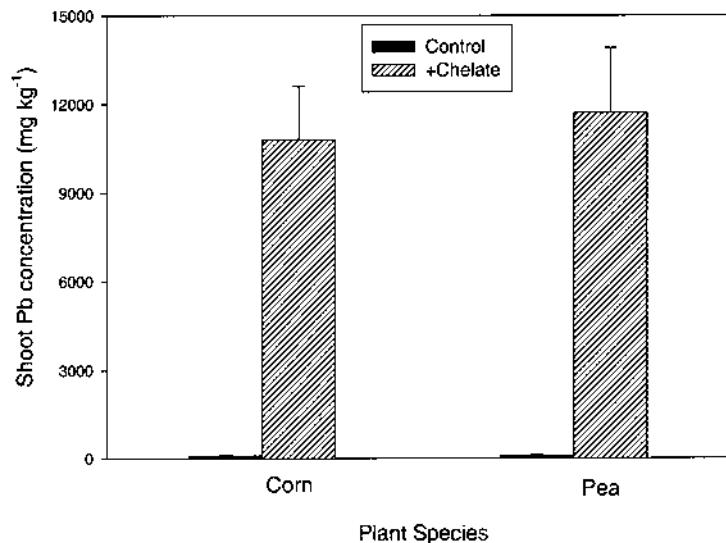
FIGURE 1   Effects of adding chelate (HEDTA, 2 g kg^{-1}) on Pb accumulation in shoots of corn (*Zea mays* L. cv. Fiesta) and pea (*Pisum sativum* L. cv. Sparkle) grown in a Pb-contaminated soil with a total soil Pb concentration of 2500 mg kg^{-1}. Control denotes the plants grown in the Pb-contaminated soil in the absence of HEDTA. Error bars represent $\pm$ SE ($n = 3$). (Adapted from Ref. 69.)
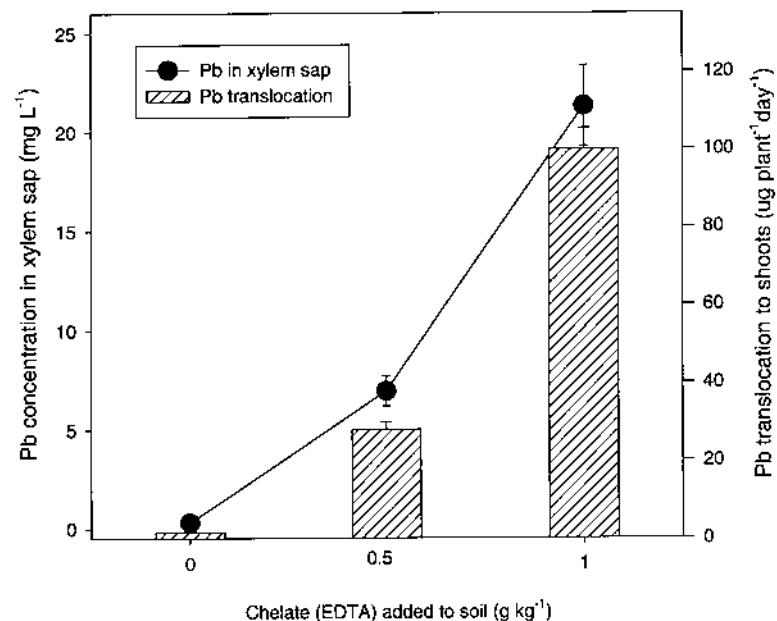
FIGURE 2 Effects of adding chelate (EDTA) on Pb concentration in xylem sap and Pb translocation from roots to shoots of 3-week-old corn plants grown on Pb-contaminated soil with a total soil Pb of 2500 mg kg^{-1}. EDTA treatment was initiated by adding the appropriate EDTA solution to the soil surface, and shoots were cut 1 cm above the root–shoot junction 24 hours after applying the chelate. Immediately following the cutting, xylem sap was collected for 8 hours for each treatment. Error bars represent ± SE ($n = 3$). (Adapted from Ref. 69.)

increase in Pb concentration in soil solution [69]. The physiological mechanism involved in chelate-triggered Pb hyperaccumulation in plants is chelate-enhanced Pb translocation. A greenhouse study demonstrated that after applications of EDTA to the root zone of plants grown in Pb-contaminated soil, Pb concentrations in shoot xylem sap increased linearly with increasing EDTA concentrations (Fig. 2). Compared with the control, addition of EDTA (1 g kg^{-1}) increased Pb translocation more than 100-fold within 24 hours (Fig. 2).

Phytoextraction of Pb from contaminated soils has been demonstrated on several sites in the United States. For example, Blaylock et al. [88] conducted a 2-year phytoremediation trial at a Pb-contaminated site in Trenton, New Jersey, using successive crops of *Brassica juncea* combined with soil amendments. After one crop, the soil Pb level in 72% of the treated area was reduced to the cleanup level (400 mg kg^{-1}) specific for residential areas [88].

Of the synthetic chelates tested so far, EDTA was the most effective one in increasing Pb desorption from soil to soil solution and Pb accumulation in plant shoots [69,73]. The chelate-triggered increase in Pb concentration of the soil solution is directly associated with the increase in Pb concentration in the xylem stream, Pb translocation from roots to shoots, and Pb accumulation in plants [13,69]. These results suggest that chelates may eliminate two major limiting factors, low Pb bioavailability and poor Pb translocation, in Pb phytoextraction from contaminated soils.

Several possible mechanisms are involved in the chelate-triggered Pb hyperaccumulation in plants [69]. First, the increase in the Pb level in soil solution by chelate is a major factor; therefore, more Pb is available to plant roots. Second, chelates could buffer Pb activity near the root surface and thereby maintain a constant supply of available Pb to root uptake sites [13,69]. Third, the Pb-chelate complex could be directly absorbed by the roots and translocated from roots to shoots [69]. Using [14]C- and ^{210}Pb-labeled EDTA and Pb-EDTA, Vassil et al. [74] confirmed that the Pb-EDTA complex was absorbed by roots and translocated to shoots. Current results indicate that phytoextraction may provide a cost-effective strategy for the cleanup of Pb-contaminated soils [13,33,88]. Environmental concerns will require that the chelate addition to the soil be minimized, and methods for preventing leaching of Pb chelates down the soil profile are required for regions where net infiltration occurs [5,69].

5.2.2 Uranium

Soil contamination with U has resulted from the development of the nuclear industry, which involved the mining, milling, and fabrication of various U products [13,32,33,89]. Uranium contamination poses serious risks to the environment and limits the future use of many sites formerly used for U production and processing. Because engineering-based remediation of U-contaminated soil is very expensive, estimated at \$2500 m^{-3} [90], phytoremediation techniques have been developed as an alternative for the cleanup of U-contaminated soils [13,32,33]. As with Pb phytoextraction, the success of U phytoextraction depends on soil U availability to plants, U uptake by roots, and U translocation from roots to shoots. To identify ideal soil amendments to increase soil U availability to plants, researchers have investigated the effect of applying synthetic chelates, inorganic acids, and organic acids on U desorption from soil to soil solution. The results of these studies demonstrate that citric acid is the most effective soil amendment to trigger rapid U desorption from soil to soil solution [32,33,89,91]. Citric acid has been shown to form a binuclear complex that increases the transport of U in the soil [92]. The high selectivity of citric acid for U is due to the high affinity of the uranyl cation (UO_2^{2+}) for carboxylate groups from citric acid [92–94].

Application of citric acid to the U-contaminated soil (total soil U 280 mg kg^{-1}) increased the U concentration in soil solution more than 200-fold [33]. In

pot experiments, the application of citric acid to the contaminated soil transiently reduced the soil pH by 0.5–1.0 unit [32,33]. The application of nitric acid or sulfuric acid at the same concentration as citric acid also reduced the soil pH by a similar magnitude. However, the increase of U in soil solution caused by nitric acid or sulfuric acid was much less than that by the citric acid [33]. The results suggest that the reduction of soil pH contributed only part of the enhanced soil U desorption. The driving force for the enhanced U desorption by citric acid is the chelation between U and citric acid. As with soil U desorption, citric acid is the most effective soil amendment in triggering U hyperaccumulation in plants [32,33]. Among the species tested so far, the citric acid–triggered U hyperaccumulation was most dramatic in *B. juncea, B. chinensis, Amaranthus cruentus,* and *Beta vulgaris* [32,33]. Shoot U concentrations in *B. juncea* and amaranth increased by more than 1000-fold in response to the application of citric acid to the U-contaminated soil containing a total of 750 mg U kg^{-1} (Fig. 3).

Uranium hyperaccumulation triggered by citric acid was so rapid that a surge of U concentration in plants was observed within 24 hours after citric acid
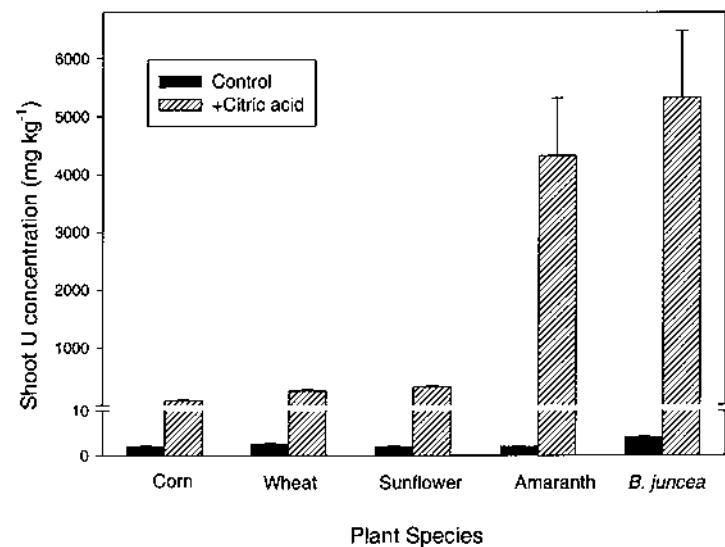
FIGURE 3 Uranium accumulation in shoots of selected plant species grown in a U-contaminated soil with total soil U of 750 mg kg^{-1} in response to the application of citric acid (20 mmol kg^{-1} of soil). Plants were grown in the U-contaminated soil for 4 weeks before applying citric acid and were harvested 1 week after the citric acid application. The control denotes the plants grown in the U-contaminated soil in the absence of citric acid treatment. Error bars represent $\pm$ SE ($n = 3$). (Adapted from Ref. 33.)

application and the shoot U concentration reached a steady state 3 days after the citric acid treatment [33]. In this form of U phytoextraction, the plants would contain a very low U concentration before the application of soil amendment. After the application of citric acid, U accumulation in plant shoots would increase rapidly, and the plants could be harvested a few days following the citric acid treatment. Uranium phytoextraction has been demonstrated at various U-contaminated sites in the United States [13,33]. This strategy has advantages in reducing the risk that might have been present by having plants with high U levels in the field for long periods of time. Applying this technique will speed up the removal of U from contaminated soils. Because citric acid is biodegradable, rapidly degrading to carbon dioxide and water [95–97], this technology represents an environmentally friendly alternative for the cleanup of U-contaminated soils.

5.2.3 Cesium 137

Radioactive cesium (^{137}Cs) contamination of soils has resulted from nuclear testing, accidental release, and nuclear energy production. Cesium 137 has a half-life of 30.2 years and has very low mobility in soils, even with high rainfall [98]. The presence of ^{137}Cs in soil and water poses significant health risk to humans and animals. There are several laboratories in universities and private companies that have studied the potential of phytoremediation for the cleanup of ^{137}Cs-contaminated soils [13,99,100]. Application of NH_4 and K to the contaminated soil significantly increased ^{137}Cs desorption from soil to soil solution and ^{137}Cs accumulation in plants [99]. Using a similar strategy for the phytoextraction of Pb and U from contaminated soils, Blaylock and Huang [13] tested effects of applying synthetic chelates, organic acid, and ammonium–potassium fertilizers on ^{137}Cs desorption from soil to soil solution. Of the soil amendments tested, ammonium fertilizers (both ammonium sulfate and ammonium nitrate) were very effective in increasing ^{137}Cs desorption from soil to soil solution. For example, after the application of 10 mmol $(NH_4)_2SO_4$ kg^{-1} to a ^{137}Cs-contaminated soil with a total soil ^{137}Cs of 370 pCi g^{-1}, the soil solution ^{137}Cs increased from 0.4 to 4.5 pCi g^{-1} [13]. The application of ammonium fertilizer increased the shoot ^{137}Cs concentration from less than 200 pCi g^{-1} for the control to more than 1200 pCi g^{-1} for both corn and winter wheat (Fig. 4).

In a field study, Lasat et al. [99] investigated the potential of three plant species (*Amaranthus retroflexus, B. juncea,* and *Phaseolus acutifolius*) to extract ^{137}Cs from contaminated soil and found a 40-fold difference in ^{137}Cs removal by the plant species tested. *Amaranthus* removed the largest amount of ^{137}Cs because of the highest ^{137}Cs concentration found in shoots and high shoot biomass produced by this species [99]. Phytoextraction of ^{137}Cs from contaminated soils has been demonstrated at the site of the Chernobyl nuclear power plant, where the accident in 1986 caused ^{137}Cs contamination of soil and water [100]. Of the 20 different soil amendments tested, ammonium salts were the most effective in in-
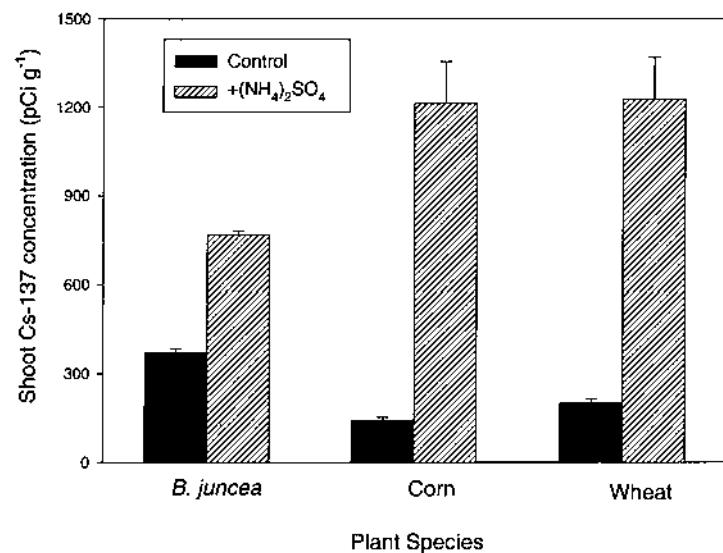
FIGURE 4 Cesium 137 accumulation in shoots of three plant species grown in ^{137}Cs-contaminated soil (total soil ^{137}Cs, 370 pCi g^{-1}) in response to the application of ammonium sulfate (10 mmol kg^{-1} soil). Plants were grown in the contaminated soil for 3 weeks before applying the ammonium fertilizer and were harvested 2 weeks after the treatment. (Adapted from Ref. 13.)

creasing ^{137}Cs desorption from soil to soil solution [100]. Of the various plant species tested, amaranth cultivars had the highest ^{137}Cs accumulation [100]. Compared with that of Pb and U, phytoextraction of ^{137}Cs from contaminated soils is a bigger challenge because the desorption of ^{137}Cs fixed into the clay minerals is very difficult. Further research is needed to identify plant species that hyperaccumulate ^{137}Cs and to identify soil and foliar amendments that enhance ^{137}Cs phytoextraction.

5.2.4 Arsenic

Arsenic is a major contaminant of soils and waters in the United States and other countries. Arsenic is a known carcinogen and mutagen, is detrimental to the immune system, and contributes to skin, bladder, and other cancers [101,102]. Currently, there is no cost-effective method to clean up As-contaminated soils. The development of a cost-effective method of removing As from soil would accelerate the cleanup process for As-contaminated soils and reduce the risk of As contamination of groundwater and drinking water. Before 1968, inorganic forms of As were used extensively in agriculture as insecticides and herbicides. Frequent application of these chemicals at high rates caused significant As accumulation in

orchard soils [103]. Inorganic forms of As have since been replaced with organic forms because of their reduced phytotoxicity and overall environmental burden. However, excessive additions of any As compounds can cause pollution of nearby ground and surface waters [104]. Arsenic concentrations as high as 500 mg kg^{-1} have been reported in soils having a history of As pesticide or herbicide applications [105,106].

Because arsenate (AsO_4^{-3}) behaves chemically similarly to phosphate (PO_4^{-3}), phosphorus fertilization of orchard soils contaminated by As increased its solubility and mobility [103]. Heavy applications of phosphate to a soil containing high As displaced up to 80% of the total As in the soil, with the water-soluble As leaching down the soil profile [105]. Increased arsenic toxicity to plants occurred following the application of P fertilizer because of As desorption from the adsorption sites by applied P [105,107]. The desorbed As is absorbed by plant roots and translocated to plant shoots and fruits, thus causing arsenic contamination of the food chain. For example, Creger and Peryea [108] reported that applications of monoammonium phosphate increased the As concentration in apple trees and resulted in severe As toxicity symptoms in these trees grown in As-contaminated orchard soils.

In many acid soils, liming is an effective method for raising soil pH and reducing aluminum toxicity. However, for soils with high As levels, increasing the soil pH could result in an increase in As movement in the soil profile because of the pH dependence of the sorption reaction of As on Fe oxide minerals [34].

Development of the As phytoremediation technology would allow in situ treatment of As-contaminated soils. The phytoextraction of As from contaminated soils could significantly reduce the risk of As contamination of the food chain and drinking water. Because complete removal of surface soils for large areas is impractical, phytoextraction technology has significant advantages for agricultural soils contaminated with low levels of As. We have studied the potential of phytoextraction of As from soils and tested the effects of applying alkalizing agents on As desorption in soil and accumulation in plants. Of the soil amendments tested, NH_4OH was effective in enhancing As accumulation in plants (Fig. 5). However, the bioaccumulation factor (ratio of shoot As concentration to soil As concentration) was much lower for As phytoextraction than for Pb and U phytoextraction. Based on the shoot As concentration in Fig. 5, the bioaccumulation factors for *B. juncea* and *B. chinensis* were less than 3. Significant improvement in this parameter is needed for effective phytoextraction of As from contaminated soils.

A research team from Dr. Lena Ma's laboratory at the University of Florida identified a fern species *(Pteris vittata)* that was able to accumulate As in the shoots to concentrations as high as 15,000 mg kg^{-1} [78]. Greenhouse studies have been conducted to investigate As accumulations in this fern along with other plant species. Preliminary data indicated that this fern accumulated, in the aboveground
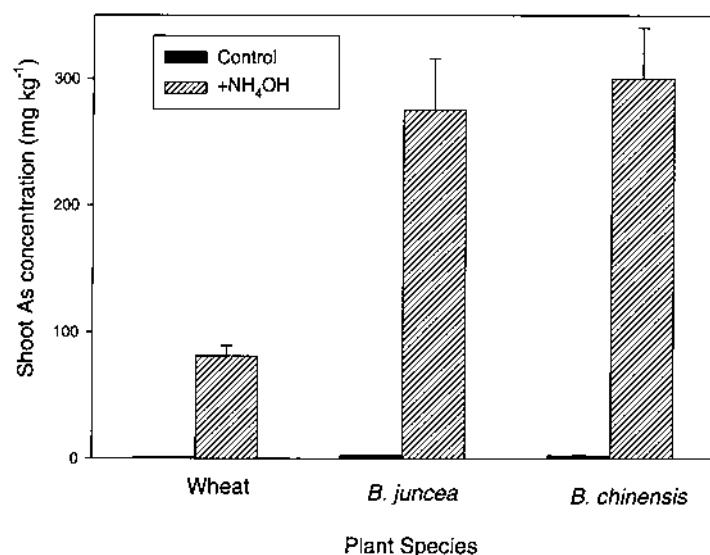
FIGURE 5 Arsenic accumulation in shoots of three plant species grown in the arsenic-contaminated soil (total soil arsenic, 110 mg kg^{-1}) in response to the application of NH_4OH (1.5 M kg^{-1} soil). Plants were grown in the contaminated soil for 4 weeks before applying the NH_4OH and were harvested 1 week after the treatment (J.W. Huang, unpublished results).

plant tissue, an As concentration more than 200-fold higher than any other plant species tested using an As-contaminated soil (J.W. Huang, unpublished results). Based on the As concentration in the soil, this fern has an As bioaccumulation factor of greater than 10 in the absence of any soil amendments (J.W. Huang, unpublished result). We are currently conducting research to demonstrate the potential of using this fern to phytoremediate As-contaminated soil and water.

6   RESEARCH NEEDS

Phytoremediation of soils contaminated by toxic metals and radionuclides has demonstrated good potential at various contaminated sites in the United States and other countries. Despite the significant progress that has been made in transferring phytoremediation technology from laboratory and greenhouse to field applications, continuous research and development are needed in a number of areas. Soil pH plays a critical role in altering contaminant availability to plants and contaminant uptake by roots. Research is needed to examine conditions under which the soil pH changes in the rhizosphere can be induced. For example, acidifying fertilizers such as ammonia sulfate can be used to reduce rhizosphere pH, and alkaliz-

ing fertilizers such as calcium nitrate can be used to increase rhizosphere pH. Plant-induced rhizosphere pH change is important because pH can alter the solubility of contaminants at root zones and enhance contaminant absorption by roots. Compared with indiscriminately acidifying or alkalizing bulk soil, the physiological change of rhizosphere soil pH will significantly reduce the risk of contaminants leaching down the soil profile. A better understanding of the mechanisms involved in soil amendment–enhanced contaminant uptake, translocation, and accumulation in the plants is needed. The elucidation of the mechanisms involved in these processes will help in the identification and possibly the synthesis of new soil or foliar amendments to accelerate the phytoremediation process.

Currently, most available metal hyperaccumulators have limitations in commercial phytoremediation because of their slow growth rate and low biomass production. Therefore, a search for hyperaccumulators that grow rapidly and produce large biomass should be continuously pursued. We should use genetics and molecular biological tools to advance phytoremediation technology. Identifying and transferring the genes responsible for metal hyperaccumulation from specific metal hyperaccumulators to plants with high biomass production could have viable commercial applications [109–111]. In addition, molecular biology has provided insights into the processes of metal uptake, translocation, and accumulation in plants. By integrating knowledge and techniques from soil science, agronomy, engineering, plant genetics, and molecular biology, we can develop an advanced phytoremediation technology to accelerate the cleanup of contaminated soils.

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